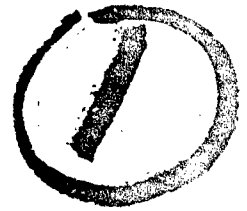


Report to the
Great Lakes Water Quality Board



AD-A149 008

**A Review of the Pollution Abatement Programs
Relating to the Petroleum Refinery Industry
in the Great Lakes Basin**

20030109004

DTIC FILE COPY

DTIC
ELECTE
S DEC 21 1984 **D**

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

84 10 02 031

Report to the
Great Lakes Water Quality Board

A Review of the Pollution Abatement Programs Relating to the Petroleum Refinery Industry in the Great Lakes Basin

by the
Petroleum Refinery Point Source Task Force
of the Water Quality Programs Committee

November 1982
Windsor, Ontario

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By <u>Per Ltr. on File</u>	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
<u>A/1</u>	



DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

DTIC
ELECTE
DEC 21 1984
S D

13 P

Preface

The Petroleum Refinery Point Source Task Force of the Water Quality Programs Committee is pleased to submit this report to the Great Lakes Water Quality Board. It includes a description of the status of the petroleum refining industry in the Great Lakes Basin and provides an overview of the historical progress (1972-1982) made by this industry to reduce its discharge of pollutants into the Great Lakes.

This report addresses the 15 refineries discharging directly to the Great Lakes Basin. It does not evaluate the refineries discharging to municipal treatment systems, other than to identify their pretreatment requirements.

Industrial representatives from the American Petroleum Institute (API) and the Petroleum Association for the Conservation of the Canadian Environment (PACE) were consulted about specific technical aspects of this industry by the Task Force in the course of preparing this report. Their contributions are appreciated.

The Great Lakes Water Quality Board has reviewed and approved the Task Force's report for publication.

Mention of trade names or names of commercial organizations in this report does not constitute endorsement by the International Joint Commission or any other government agency.

Table of Contents

TITLE	PAGE
PREFACE	iii
LIST OF TABLES	ix
PREAMBLE	1
CONCLUSIONS	3
RECOMMENDATIONS	5
STATUS OF THE PETROLEUM REFINERY INDUSTRY	7
Industry Overview	7
Refinery Processes	9
Refinery Wastewater Characteristics	9
Wastewater Treatment	10
POLLUTION ABATEMENT PROGRAMS IN CANADA	11
Federal Programs	11
Ontario Programs	12
POLLUTION ABATEMENT PROGRAMS IN THE UNITED STATES	15
Federal Programs	15
Wisconsin Programs	16
Michigan Programs	17
Ohio Programs	18
Indiana Programs	18
New York Programs	19
EFFLUENT LIMITATIONS	21
In Canada	21
In the United States	22
Industry Surveys	23
Sampling and Analysis Program	24
Treatment Technology Evaluation	24
ANALYTICAL PROTOCOLS	27
SELF-MONITORING AND FEDERAL/STATE/PROVINCIAL INSPECTION PROGRAMS .	29
Indiana	31
Wisconsin	31
Ohio	32
New York	32
Michigan	32
Ontario	32
Summary	33

TABLE OF CONTENTS (CONTINUED)

TITLE	PAGE
DISCHARGE TRENDS	35
COMPLIANCE	39
Ontario	39
Ohio	43
Indiana	43
Wisconsin	43
New York	43
Michigan	43
Summary	44
AREAS OF CONCERN	45
Grand Calumet River and Indiana Harbor Ship Canal	46
Saginaw River System and Saginaw Bay	46
St. Clair River	47
Maumee River	49
St. Louis River, Minnesota	49
Summary	50
TOXIC AND NONCONVENTIONAL POLLUTANTS	51
OIL SPILL PREVENTION	57
In Canada (Ontario)	57
In the United States	57
SOLID WASTE DISPOSAL	61
United States	61
Canada	62
Ontario	63
Wisconsin	63
New York	63
Indiana	63
CLOSING OF REFINERIES	65
GLOSSARY OF TERMS	67
TERMS OF REFERENCE - PETROLEUM REFINERY POINT SOURCE TASK FORCE . .	69
MEMBERSHIP LIST - PETROLEUM REFINERY POINT SOURCE TASK FORCE . . .	71

TABLE OF CONTENTS (CONTINUED)

APPENDICES	TITLE	PAGE
I.	A List of Petroleum Refineries Discharging into the Great Lakes Basin, 1981	75
II.	Intermediate and Finished Products Produced by the by the Petroleum Refining Industry	85
III.	Summary Description of Major Wastewater Sources in Refineries	87
IV.	A List of Petroleum Re-Refineries Located in the Great Lakes Basin	93
V.	Canadian Effluent Limitations - Federal and Ontario . . .	95
VI.	Toxic and Nonconventional Pollutants Under Investigation in the United States Screening Program.	99
VII.	United States Effluent Guidelines	103
VIII.	Analytical Protocols	105
IX.	Summary of U.S. EPA Screening Program Data	107
X.	List of Parameters Selected for Canadian Refinery Survey.	123
XI.	Frequency of Detection and Concentration Range of Organic Substances	125
XII.	Summary of Identified Sources of Refinery Solid Waste Streams	127
BIBLIOGRAPHY		137

BLANK PAGE

List of Tables

	PAGE
TABLE 1. DESIGN PROCESSING CAPACITY OF PETROLEUM REFINERIES DISCHARGING TO THE GREAT LAKES BASIN - NOVEMBER 1, 1982	8
TABLE 2. RESULTS OF DISCHARGE MONITORING REPORT - QUALITY ASSURANCE SAMPLING PROGRAM FOR GREAT LAKES BASIN PETROLEUM REFINERIES	30
TABLE 3. SUMMARY OF DISCHARGE TRENDS OF POLLUTANTS FROM PETROLEUM REFINERIES IN THE GREAT LAKES BASIN	36
TABLE 4. PETROLEUM REFINERY COMPLIANCE SUMMARY FOR 1980	40
TABLE 5. PETROLEUM REFINERIES DISCHARGING TO AREAS OF CONCERN	45
TABLE 6. SUMMARY OF SAMPLING AND ANALYSIS STUDY RESULTS OF TOXIC POLLUTANTS	52
TABLE 7. SUMMARY OF RESULTS FOR CONVENTIONAL AND NONCONVENTIONAL POLLUTANTS	55


BLANK PAGE

Preamble

In 1972 the Governments of Canada and the United States entered into an Agreement on Great Lakes Water Quality. This Agreement was renewed in 1978 with the main purpose of restoring and maintaining the chemical, physical, and biological integrity of the waters of the Great Lakes Basin ecosystem.

Under Article VI 1(b) of the 1978 Agreement, the Parties agreed to continue to develop and implement programs "for the abatement, control and prevention of pollution from industrial sources entering in the Great Lakes System." One of the tasks of the Great Lakes Water Quality Board is to report regularly on the progress of industry in controlling pollution. In 1977 a subcommittee of the Board prepared a special report on three major polluting industries, one of which was petroleum refining (Appendix C, Remedial Programs Subcommittee Report to the Great Lakes Water Quality Board, IJC, 1977). In 1982 the Water Quality Programs Committee established a Petroleum Refinery Task Force to review the implementation and the results of the regulatory programs for that industry.

— This report describes the findings of the Task Force regarding effluent quality improvement, analytical protocols, trends of pollutant loading, and compliance with jurisdictional effluent limitations. It also discusses the petroleum refineries located in Areas of Concern, as defined by the Board. In summary, the Task Force concludes that since 1976 there has been a significant improvement in the quality of the wastewater being discharged from petroleum refineries to the Great Lakes Basin. It also believes that additional efforts should be made to evaluate the possible long-term adverse effects of potentially toxic substances known to be present in refinery effluents in low quantities.



BLANK PAGE

Conclusions

The Task Force reviewed the progress made by the petroleum refining industry to reduce its pollutant discharges in response to pollution abatement programs and concluded that:

1. Based on the present evaluation, it is the opinion of the Task Force that the jurisdictional programs as they relate to the petroleum refining industry are adequate to meet the general program requirements of Article VI, Section 1(b) of the 1978 Agreement.
2. A significant improvement in the quality of wastewater being discharged from Canadian and United States refineries has been observed since 1976. This improvement has occurred both on a basis of total load and on a basis of loading per unit of crude oil processed, and is a result of efforts by the industry to meet the applicable requirements imposed by the jurisdictions. This improvement has been primarily achieved by upgrading treatment facilities, and by improved water management.
3. Overall, the petroleum refining sector generally meets the discharge requirements imposed by the jurisdictions. However, the majority of the refineries do have occasional incidents for one or two parameters, and a few have frequent instances of exceeding these requirements.
4. There has been a 10% reduction in crude oil processed in the 1976-1981 period in the Great Lakes Basin. Depending on demand and economic climate an additional reduction in crude processing may take place during the next several years, but this reduction is not expected to have a major impact on refinery waste loadings to the Great Lakes.
5. All refineries discharging to the Great Lakes Basin have treatment facilities which include biological wastewater treatment systems. Studies on the petroleum refinery industry have shown that a well operated biological treatment system significantly reduces conventional pollutants as well as many toxic substances present in refinery wastewater. However, the treated effluent from refineries still contains certain toxic organic and metal substances at very low concentrations.
6. Routine monitoring for most toxic substances is not a jurisdictional requirement. The information base on toxic substances in refinery effluents has been generated from the industry as a whole and is not specific to the refineries in the Great Lakes Basin. It is expected that the effluent characteristics for the refineries in the basin would be similar to those surveyed.

7. A detailed comparison of jurisdictional requirements for pollutants discharged by the industry was not addressed as it would have involved a detailed refinery-by-refinery comparison. Both countries have adopted similar strategies for controlling water pollution from the petroleum refining sector. It is the opinion of the Task Force that major differences do not exist, as supported by the installation of similar pollution control technology.
8. The refinery effluent treatment systems currently in use are sophisticated and require well trained personnel to run at maximum efficiency. Most states with refineries in the Great Lakes Basin require certified operators to control these systems.
9. The Task Force considered the quantities of wastewaters being generated by the re-refineries in the basin. The chemical characteristics of effluent data were not readily available; however, the process water component of these wastewaters is known to be very small in volume, and the re-refiners generally discharge to municipal wastewater treatment plants. Based on the limited data available to the Task Force no attempt was made to review them in detail.
10. Petroleum refineries are not significant contributors of phosphorus loading to the Great Lakes Basin. Phosphorus is added to promote the biological activity in biological waste treatment systems and, subsequently, most of this phosphorus is consumed by the biomass which accumulates in the sludge.
11. The individual impact of a refinery discharging to an area of concern cannot be evaluated without the consideration of other dischargers in the area.
12. Petroleum refineries generally do not have specific requirements to minimize the environmental impacts of thermal discharges in the Great Lakes Basin. One refinery in Ohio has thermal control requirements because of local site-specific conditions.
13. There are no requirements specific to refineries to minimize the adverse environmental impact of water intakes. Refineries are not the most significant users of water, when compared to other industrial sectors.

Recommendations

The Petroleum Refinery Point Source Task Force recommends to the Water Quality Board that:

1. The long-term impact of some of the persistent toxic substances in the refinery effluent discharges be determined in any water quality and/or chronic toxicity studies being conducted, particularly in the Areas of Concern.
2. Refineries discharging into the Great Lakes Basin be encouraged to characterize their effluent for the most significant toxic substances by periodic monitoring.
3. The jurisdictions modify their existing requirements if these studies indicate that previously unknown adverse effects exist, particularly in the Areas of Concern, due to refinery effluents.
4. The jurisdictions examine the procedures for plant closing and determine their adequacy.
5. Ohio and Ontario investigate the benefit of and the need for a certified wastewater treatment plant operator program for industry.
6. Additional efforts be made to standardize and improve analytical protocols, used by the jurisdictions in testing for the presence of organic compounds, particularly in industrial effluents. This is essential to a meaningful comparison of data on trace contaminants.
7. Refineries experiencing difficulties in meeting effluent requirements improve the operation of their existing wastewater treatment facilities, continue to optimize and upgrade these facilities, and incorporate process modernization techniques, including improved water management and recycling of process waste.
8. Problems identified in Areas of Concern be addressed by a waste load characterization procedure, in order to determine the relative magnitude of the refineries' contributions, and that specific problems be corrected on a case-by-case basis such as using a waste load allocation procedure or other means.

Status of the Petroleum Refinery Industry

INDUSTRY OVERVIEW

There are a total of 322 petroleum refineries, with a combined refining capacity of 2.8 million cubic meters (17.5 million barrels) per stream-day, in Canada and the United States.

The United States, with 285 refineries, has most of its 2.4 million cubic meter (15 million barrels) per stream-day refining capacity concentrated in major crude production areas, such as, Texas, California, Louisiana, Oklahoma, and Kansas; and major population areas, such as Pennsylvania, Illinois, Ohio, New Jersey, and Indiana.

Canada, with 37 refineries and a crude capacity of 0.4 million cubic meters (2.5 million barrels) per stream-day, has 59% of its refining capacity located in Ontario and Quebec. Alberta, the major production area, has about 12% of the refining capacity.

A typical refinery represents a capital investment of 500 to 750 million dollars. The average refinery employs 400 to 500 skilled and professional workers and has a monthly payroll of about one million dollars. Contract maintenance totals several million dollars per year, and locally purchased services and supplies may amount to another twelve million per year. Local and state/provincial property taxes are about 1.5 million dollars per year or more.

Since the mid-70's, consumption of petroleum products in the United States has decreased by over 20%. Recently, demand has been level, and no further decreases are expected. In Canada, consumption has decreased 6% from 1980 to 1981, with another 2% decrease expected in 1982. In Ontario, consumption is expected to decrease at a faster rate, and this has prompted Shell Oil to close its Oakville refinery in early 1983. The industry in both the United States and Canada project no new refinery construction in the near future in the Great Lakes Basin.

The Great Lakes Basin contains 5% of the United States and 32% of the Canadian refinery capacity. This report addresses the 15 refineries discharging directly to the Great Lakes Basin. Table 1 lists the total number of refineries in each jurisdiction and includes information on their total crude refining capacity. Appendix I contains specific information on individual refineries. This report does not explicitly address those refineries* discharging to municipal treatment systems other than to identify their pretreatment requirements.

*Crystal Refining Company, Carson City, Michigan and Marathon Oil Company, Detroit, Michigan.

TABLE 1. DESIGN PROCESSING CAPACITY OF
PETROLEUM REFINERIES DISCHARGING TO THE GREAT LAKES BASIN
NOVEMBER 1, 1982

Jurisdiction	Total No. of Plants	Total Direct Dischargers	Crude Capacity	
			1000 m ₃ / Stream-Day	(1000 bbls/ Stream-Day)
INDIANA	1	1	66.7	(420)
MICHIGAN				
Direct Discharge	2	2	7.2	(45)
Discharge to POTW*	2	-	11.4	(72)
OHIO	3	3	49.1	(309)
WISCONSIN	1	1	6.0	(38)
	—	—	—	—
Total U.S.	9	7	140.4	(884)
ONTARIO	8	8	122.1	(768)
	—	—	—	—
Total Great Lakes Basin	17	15**	262.5	(1,652)

*Publicly Owned Treatment Works

**This report addresses only these refineries. For purposes of discharge trend comparison and compliance evaluation, refineries that have either ceased operation or discharge their process water to a POTW are sometimes included when referring to historical data. These exceptions are noted in the report.

REFINERY PROCESSES

The basic function of a refinery is to process crude oils into the variety of petroleum products required by an industrialized society. These include such products as gasoline, fuel oil, heating oil, and solvents. Moreover, it is important to note that a typical refinery produces petrochemical feedstocks that are the basis for a myriad of products from other industries including plastics, synthetic rubbers, synthetic fibers, pharmaceuticals, detergents, pesticides, fertilizers, explosives, and many more.

The first process step in a refinery consists of physically separating crude oil into a number of fractions of varying molecular weights by distillation. Subsequent conversion processes are then required for intermediate and final products. Although more than 150 separate processes have been identified in the industry, they can generally be classified as physical separation and/or chemical conversion operations. Distillation, liquid extraction, and crystallization are examples of common physical separation processes. Cracking, reforming, and alkylation are some of the major chemical conversion processes used. Finished products are manufactured by blending various intermediate products in the required proportions. Appendix II lists the products produced by the industry and Appendix III contains an example of a typical refinery process flow diagram with explanations of the various processes that produce waste water.

Petroleum re-refineries and recovery plants produce a variety of specialty products from processed petroleum products. These dischargers use small quantities of water (mainly for cooling) and do not generate process wastes comparable to refineries. Therefore, this report does not address this industrial category other than to list those located in the Great Lakes Basin (Appendix IV).

REFINERY WASTEWATER CHARACTERISTICS

A wide range of organic and metal pollutants can be found in refinery wastewaters. Many of the contaminants originate from the crude oil while others are produced in the process units. Others are the products of corrosion or additives, catalysts, and chemicals used in the operation.

As oil is the main constituent of the manufacturing operation, it is the most common contaminant encountered in the wastewater streams. In addition to oil, wastewaters contain varying concentrations of other contaminants such as sulphides, mercaptans, cyanides, inorganic salts, suspended solids, benzene derivatives, other hydrocarbons, and heavy metals. Phosphorus is also present in biologically treated refinery wastewater, but in low concentrations, typically at levels near 0.5 mg/L. Phosphorus is added, usually in the form of phosphoric acid, to the process waste stream prior to biological treatment as a required nutrient for biological activity. The phosphorus is subsequently consumed by the biomass which accumulates in the sludge. Some typical discharges from a refinery would be on the order of .5 to 3 kg/day phosphorus, although one Ohio refinery has reported a discharge of 14.4 kg/day phosphorus. This is discussed further in the Areas of Concern section. For purposes of comparison, the total load of phosphorus from municipalities in the Great Lakes Basin was 18,700 kg/day in 1981.

The quantities and types of wastewaters generated by each plant's total production mix therefore varies as it relates to the nature of the crude and the variety of processes used as well as many other factors not specific to the refining industry, such as water usage, plant age, practices, etc.

WASTEWATER TREATMENT

To minimize the waste discharges of the pollutants or contaminants described in the previous section, the refinery industry employs a variety of treatment practices and technology. Practices such as sour water stripping and oil/water emulsion breakage using heat provide varying degrees of oil recovery, sulfur removal, and phenolic reduction. Contaminated wastewaters are normally segregated from non-contaminated waters (such as once-through-cooling-water) and then treated according to their oil chemical and solids make-up. The most prevalent treatment processes in use are settling and air flotation to remove solids and oils (primary treatment); and chemical and/or biological oxidation to remove dissolved chemical contaminants and reduce biological oxygen demand (secondary treatment).

Tertiary treatment, such as carbon adsorption and additional filtration, is used at some refineries. Appendix III contains an example of a typical refinery wastewater treatment system.

Depending upon location, size and applicability a few refineries also dispose of wastewater in deep-wells constructed in suitable geological formations. A number of refineries discharge their wastewaters to municipal waste treatment facilities.

Pollution Abatement Programs in Canada

The responsibility for environmental protection in Canada is shared between the federal and provincial governments. The Canada-Ontario Agreement on Great Lakes Water Quality (COA) provides a vehicle for cooperative environmental management in Ontario and the Great Lakes Basin, in addition to other federal and provincial programs.

The federal government, in consultation with the provinces and industry, has developed national baseline effluent regulations and guidelines for specific industrial sectors including the petroleum refining industry. The Ontario Government enforces the federal requirements as minimum standards.

FEDERAL PROGRAMS

The Fisheries Act and the Environmental Contaminants Act are the federal laws under which Environment Canada responds to the requirements of the Great Lakes Water Quality Agreement.

Petroleum Refinery Effluent Regulations and Guidelines (January 1974) stipulate national baseline standards based on Best Practicable Control Technology (BPT). The Regulations are a legal requirement, pursuant to Sections 33 and 34 of the Fisheries Act, effective November 1, 1973. They apply to all new refineries commencing operation after this date. The Guidelines are a code of good practice, not written into law, which apply to all existing refineries in operation prior to November 1, 1973. In addition, there are guidelines for testing the acute toxicity of effluents from both new and existing refineries.

With increasing concern over toxic* substances, Environment Canada and the Petroleum Association for Conservation of the Canadian Environment (PACE) have cooperated in joint studies on the determination and characterization of toxic compounds in refinery effluents. Studies have been completed which characterize the effluents from a broad cross-section of the refining industry in Canada. A longer-term project at an individual refinery was designed to reveal the variability of toxic components being discharged. Additional work is being planned to determine the fate of toxic compounds in refinery effluents and wastewater treatment systems.

Environment Canada and the Ontario Ministry of the Environment conducted a joint study of toxic compounds in industrial effluents in the St. Clair River area in 1979-81, which included four petroleum refineries. One facet of this study was an in-depth evaluation of a refinery wastewater treatment plant with tertiary treatment (carbon adsorption).

*Hereafter referred to as toxic pollutants, substances, or compounds even though not necessarily present at toxic concentrations, levels, or amounts.

ONTARIO PROGRAMS

Ontario began its efforts to control water pollution from the petroleum industry in 1956. Since petroleum refineries are located in areas where the shoreline waters are used for swimming, boating, fishing, and as a source of potable water, the Ontario Water Resources Commission issued strict effluent concentration objectives for five pollutants. These pollutants were oil and grease, phenols, suspended solids, pH, and Biochemical Oxygen Demand.

To meet these objectives, the petroleum industry was expected to install some combination of the following:

- strippers to remove hydrogen sulphide and ammonia;
- separate sewers, neutralizing facilities and recovery systems for chemicals used to treat refinery products;
- segregated sewers for process/oily waters and stormwaters;
- individual gravity oil separators for each waste stream and flow surge quality equalization ponds for the combined effluent;
- continuous pH control;
- an oil flotation unit for oil separation and some H₂S stripping; and
- a biological treatment unit with clarifier.

During 1956-1963, the two new refineries built on Lake Ontario met these objectives. The original owner of the British Petroleum Refinery, Cities Services, had a fish pond at the end of the treatment system. Several upsets killed the fish before the treatment system could be modified. Although the fish pond was not restocked, this refinery effluent passed both the 24- and 96-hour static fish tests. The Shell Refinery at Oakville was innovative in reducing spills from its product blending area. Both refineries are low water users. Compliance programs were developed with the remaining five refineries built prior to 1955. In 1974 the Commission became part of the Ministry of the Environment.

In 1974 the compliance schedules were accelerated to meet federal requirements. The basic effluent treatment systems were in place at all refineries by 1975. Increased effluent monitoring requirements as specified in the Federal Guidelines were in effect by February 1974. Industry has continued to report these self monitoring results to the Ministry. These monitoring requirements include a monthly 24-hour static fish toxicity test. A joint effort by the federal and provincial agencies verifies these tests with a 96-hour static fish toxicity test for each refinery annually.

With the signing of the 1978 Great Lakes Water Quality Agreement, the Ministry updated the effluent concentration objectives to include limits for ammonia. Also, effluent concentration objectives for trace metals in the cooling water were issued. (See Appendix V for the objectives from Ontario's Liquid Effluent Guidelines for the Petroleum Refining Industry.)

Under provincial legislation, the Ontario Ministry of the Environment employs a variety of measures to effect compliance with its requirements. The Ministry's pollution abatement policy clearly delineates the use of Control Orders, Requirements and Directions, Program Approvals, and provides for prosecution. When any one of these tools is used, the public is informed of the requirements. Local circumstances can be considered while meeting the Province's environmental objectives.

In Ontario a Certificate of Approval may contain a condition prohibiting the creation of a thermal barrier that inhibits the migration of fish and other aquatic life. No problems have been identified with thermal barriers at Ontario refineries.

Since March 29, 1961 a permit has been required for the withdrawal of water in Ontario. The location and design of the proposed intake is reviewed by the Ministry's staff to ensure that fish entrainment is minimized. All Ontario refineries have screens and bars as part of their intake structures. For new refineries with low water usage, these devices are adequate, but there have been some problems at the older refineries which use once through cooling water.

The Ministry makes regular biological surveys of receiving water bodies to confirm improvements in effluent quality. In the Sarnia area, petroleum refiners, petrochemical plants and other chemical plants discharge into the St. Clair River. The bottom fauna of the St. Clair River were studied in 1968 and 1977. A comparison of the results found a major improvement in water quality as indicated by an increase in the number and variety of pollution sensitive organisms and by a decrease in the area of severely degraded water quality. These studies indicated that efforts to control chlorinated organics and heavy metals are succeeding and therefore should continue.

In 1977-78, in response to the Great Lakes Water Quality Agreement, a study of trace organics in the St. Clair River - Lake St. Clair system was completed. New analytical techniques using mass spectrometry and gas chromatography were developed and refined for this study at the Ministry's Central Laboratory in Toronto.

Pollution Abatement Programs in the United States

FEDERAL PROGRAMS

Programs for pollution abatement in the United States are administered according to the Federal Water Pollution Control Act (FWPCA). The 1972 amendments to this Act require the U.S. Environmental Protection Agency (EPA) to develop effluent limitations (guidelines) on a national scale for various industrial categories. In this program each direct discharger must obtain a National Pollutant Discharge Elimination System (NPDES) permit from the federal government directly or indirectly via the state in which the discharge will occur. NPDES permits, issued for a maximum of five years, include qualitative and quantitative limitations for the discharge of pollutants. These permits also include self-monitoring requirements to ensure compliance with these limitations. When necessary, a compliance schedule is specified, outlining dates for the construction of facilities or for other means of meeting the limitations. In situations where NPDES permits have expired and have not been re-issued in a timely manner, federal and state administrative procedures provide that the terms and conditions of the expired permit remain in effect until a new permit is issued.

The FWPCA proposed a bipartite process for reducing the discharge of pollutants: dischargers would apply Best Practicable Control Technology available (BPT) by July 1, 1977, and Best Available Technology economically achievable (BAT) by July 1, 1983 (revised to July 1, 1984).

Amended in December 1977, the FWPCA became known as the Clean Water Act; its focus was the control of toxic pollutants. In contrast to its forerunner, the Clean Water Act classified industrial pollutants in three categories: conventional, toxic and nonconventional. In the 1972 Act conventional pollutants included BOD₅, suspended solids, fecal coliform and pH; EPA later added oil and grease. In a Court settlement between EPA and the Natural Resources Defense Council in 1976, 65 substances and categories were designated toxic. These "toxics" were subsequently broken down to 129 specific pollutants. The Clean Water Act focused on these 129 specific pollutants whose numbers may be increased or diminished by EPA after it has notified the public and considered their comments. The final category, nonconventional pollutants, are the remaining substances which are not identified as toxic or conventional. By July 1, 1984, industrial discharges must meet existing guidelines by utilizing Best Conventional Pollutant Control Technology (BCT) for conventional pollutants, and BAT for toxic and nonconventional pollutants. These guidelines are minimal requirements. More stringent restrictions may be imposed to maintain the specified standard for receiving water or to support stricter state effluent standards. New source performance standards (NSPS) are required for new industrial dischargers at

the commencement of operation, and are to be based on the "best available demonstrated control technology, processes, operating methods, or other alternatives including, where practicable, a standard permitting no discharge of pollutants." For indirect dischargers which are industrial facilities that discharge pollutants to publicly owned treatment works (POTW), the Clean Water Act directs U.S. EPA to establish national pretreatment standards for pollutants that are not compatible with municipal treatment plants. The Clean Water Act requires that pretreatment standards for existing sources (PSES) be achieved within three years of promulgation, and pretreatment standards for new sources (PSNS) be achieved upon commencement of operation.

The control of thermal discharges is addressed by Section 316(a) of the Clean Water Act and by temperature limits developed in the various state water quality standards. Section 316(a) allows relaxed temperature limits for thermal discharges which have not been shown to adversely affect receiving waters.

Petroleum refineries have historically used large quantities of water for once-through process cooling. Most newer refineries utilize cooling towers and other equipment to recycle their cooling water. This greatly reduces the volume of their thermal discharge and the constant need for fresh water.

Where thermal discharges, including those of petroleum refineries, have been shown to cause adverse impacts they have been required to reduce their thermal load or relocate their discharge so that it can be diluted and cooled before it causes a significant impact. An example of this latter modification is the relocation of the thermal discharge at the Standard Oil Refinery at Toledo. In Otter Creek, the thermal discharge was confined, forming a thermal barrier to fish passage up the creek. In Maumee Bay, wind and current will assist a jet diffuser in rapidly dissipating the thermal discharge.

Section 316(b) of the Clean Water Act and similarly worded state regulations require the design, location, construction and capacity of cooling water intakes to reflect best available technology for minimizing adverse impact to aquatic life. Where water intakes have been shown to significantly impact aquatic life by impingement and/or entrainment they have been required to install modifications to control or eliminate the problems. To date, no petroleum refinery cooling water intake has been identified as a problem.

WISCONSIN PROGRAMS

Wisconsin borders Lake Superior and Lake Michigan. The one petroleum refinery in the state discharges to the Lake Superior basin. A reprocessing plant which discharges to the Lake Michigan basin is also located in Wisconsin.

The Wisconsin Department of Natural Resources was granted approval of their Pollutant Discharge Elimination System permit program in 1974. Wisconsin permit law includes groundwaters as well as surface waters, and therefore, discharge permits are required for land disposal. The Department of Natural Resources applies appropriate effluent limits based on BPT for the refinery industry, unless there are more stringent water quality requirements. This is the case for the one petroleum refinery in the state, and limitations based on state water quality standards have been applied for BOD₅ and NH₃-N.

MICHIGAN PROGRAMS

Michigan has over 100,500 square kilometers (38,800 square miles) of Great Lakes within its boundaries. All petroleum refineries and petroleum re-refineries in this state discharge the great majority of their wastewater into the Great Lakes Basin. Some wastewater is disposed of into various bedrock formations using deep disposal wells. Two refinery facilities discharge their process wastewaters directly into natural surface waters tributary to the Great Lakes. Another two refineries and one re-refinery discharge into municipal systems for the treatment of their wastewaters. None of the refineries discharge directly into the Great Lakes.

The Michigan Water Resources Commission has the authority to protect the water resources of the state, including the Great Lakes. Early efforts prior to the 1970s were directed towards the protection of inland streams from discharge, and spillage of crude oil and refinery products. The mechanism for achieving this was by issuance of commission orders and stipulations.

Michigan was one of the first states to receive authority from the U.S. EPA to issue NPDES permits. By late 1977, all the refineries were in compliance with the effluent limitations of their NPDES permits.

The Michigan Department of Natural Resources has developed the Critical Materials Register (CMR) to provide the foundation for the Overall Toxic and Hazardous Material Management Program. The CMR is a list of substances of high environmental concerns. Michigan industries must report annual use and discharge of these toxic substances if they discharge to waters of the state or to POTWs. Information from CMR, integrated with existing pollution control programs, is used to better control toxic substances use and discharge.

Section 5 of Act 245, Public Acts of 1929, as amended, provides Michigan with the ability to make rules and orders restricting the polluting content of any waste material or polluting substance discharged or sought to be discharged into any lake, river, stream, or other waters of the state. Further, Rule 57 of this Act provides the mechanism for restricting toxic substances (a polluting substance) in the wastewater discharge.

Act 245 also provides Michigan with an industrial wastewater treatment plant operators' certification program. This program requires that every facility, with a wastewater discharge to the surface or groundwaters have their treatment systems under the direct control and supervision of an operator certified by the state. Furthermore the monthly operation reports, required by a permit, must be signed by the operator attesting to the accuracy of the data.

The operators are certified by written examination. The certification requirements vary according to the complexity of the treatment system. Many certifications, including those for a biological treatment system, require experience plus advanced education.

The purpose of the program is to ensure that these treatment systems will receive the attention and care that a highly skilled operator can provide.

Having such an operator in responsible charge of the system will guarantee that a knowledgeable person will be available to make the necessary day to day adjustments so that the final effluent will be in compliance with the permit limitations.

Many water treatment additives are used for controlling scale, corrosion, and biological growths in cooling water and stream generating systems. The additives often contain toxic substances which could have an adverse impact on the waters of the state if discharged in unrestricted quantities. In Michigan a discharger proposing to use these materials may be required to demonstrate that the additive will not exceed certain water quality based effluent limits placed in their permit.

Furthermore, the discharger must demonstrate that this use of an additive will not place exposed humans to an unacceptable level of risk when the additive is known to contain (or is known to be transformed into) a chemical which is a human or animal carcinogen, confirmed genotoxic teratogen, or confirmed hereditary mutagen.

OHIO PROGRAMS

Pollution abatement of the petroleum refining industry is based on federal effluent guidelines and Ohio water quality standards. Effluent limitations in the NPDES permits for Ohio oil refineries seldom differ from those specified by federal guidelines, however, temperature, BOD₅, and NH₃-N limits are often more stringent, reflecting site specific water quality considerations.

The initial round of permits included compliance schedules requiring BPT by July 1, 1977. In 1979 the U.S. EPA proposed BAT limits for the industry which have not been finalized. Renewal of existing NPDES permits is being withheld pending the issuance of BAT guidelines provided that the permittee is in compliance with BPT, and there is no evidence of water quality or toxics problems. In the case of noncompliance or the presence of water quality or toxics problems, Ohio can issue permit renewal based on water quality standards and Best Professional Judgement (BPJ) for toxics.

Since the mid 1960s Ohio's oil refineries have been installing new equipment and upgrading existing facilities to reduce their effluent loadings. This effort has resulted in a generally high level of compliance.

INDIANA PROGRAMS

Indiana began its major effort for pollution abatement of the petroleum refining industry in the 1960s. The goal of the program was the achievement of water quality as defined by Indiana's water quality regulations for Lake Michigan and its tributaries. With the development of the NPDES permit program, effluent limitations for refineries were established in discharge permits based upon federal effluent treatment guidelines and/or water quality standards.

Indiana has four types of permits which industries may be required to obtain: NPDES permits; construction permits for the construction of new facilities or additions to existing facilities; operation permits for the operation of on-line facilities where the wastewater or the operation techniques may threaten the environment; and land application permits for the land application or disposal of wastewater or sludge. Provisions for obtaining these permits are provided in 331 IAC 3.1 through 5. An NPDES permit satisfies the requirement of the operation permit.

NEW YORK PROGRAMS

In anticipation of administering the FWPCA, New York State modified its Environmental Conservation Law to conform to the federal law. In 1975 the State was granted authority to administer the federal permit program. Petroleum refineries with direct surface water discharges into the Great Lakes Basin have been issued NPDES permits. Refineries discharging into POTWs are regulated indirectly by the permit of the municipality. Permits issued by New York currently contain limitations for BPT, water quality limits for conventional pollutants, and water quality limits for certain toxic pollutants.

Effluent Limitations

United States effluent limitations are based primarily on process subcategories and crude processing capacity while Canadian effluent limitations are based on the refineries' reference crude rate, time of start-up and process alterations.

A direct comparison of effluent limitations between U.S. and Canadian refineries would involve an exhaustive refinery-by-refinery study. Process categorization, monthly crude rates, refinery start up and alterations are some of the factors that would then need to be addressed for each refinery in attempting a comparison of the limitations. One very important and overriding aspect of the effluent limitations is that the application of these jurisdictional requirements has resulted in the installation of similar pollution control technology for the refineries. Specifically, biological treatment facilities are installed in all refineries discharging directly to the Great Lakes Basin. Since the application of these effluent limitations has in fact resulted in such similar control technology being employed, it was the opinion of the Task Force that a direct comparison of jurisdictional requirements was not merited.

A discussion of the effluent limitations for each country is presented below.

IN CANADA

The Federal Petroleum Refinery Regulations and Guidelines limit the discharges of substances which are deleterious to fish. The controlled substances are: oil and grease, total suspended solids, phenols, sulphides, and ammonia. Limits are also prescribed for pH and acute toxicity to Rainbow Trout. Only those waste streams which discharge directly to surface waters are taken into account. The more strict limits applied to the expanded portion of an expanded refinery and the altered portion of an altered refinery are equivalent to those imposed on new refineries (see Appendix V, Definitions).

The aim of both the Regulations and Guidelines is to ensure that all refineries operating in Canada apply best practicable treatment technology.

The authorized deposits of deleterious substances in both the Regulations the Guidelines are based on the refinery's reference crude rate (RCR), which is the average daily throughput of crude, over a specified period (not necessarily design capacity), declared by the company. When the actual average throughput varies for more than two months by greater or less than 15% of the RCR, a revised RCR must be declared. The authorized deposits are subcategorized on a monthly basis as:

1. Monthly Amount

The arithmetic mean of the daily loading of a limited substance. This limit may not be exceeded without incurring a violation or exceedence.

2. One Day Amount

This allowance may be exceeded once per month.

3. Maximum Daily Amount

This limit may not be exceeded.

The two latter limits are based on daily deposits and allow for temporary upsets in the wastewater treatment system. The limit for pH is a range of 6.0 to 9.5.

In keeping with Section 33 of the Fisheries Act, which is intended to protect surface waters inhabited by fish, guidelines for conducting toxicity tests on refinery effluents were also published. The fish toxicity test was intended to eliminate the need to monitor parameters for which federal effluent limits have not been established. These include BOD₅, COD, and heavy metals in process effluent and once-through cooling water.

Additional loading allowances are granted under the Regulations and the Guidelines for oil and grease, volatile suspended solids, and phenols contained in stormwater runoff (see Appendix V).

Ontario issued effluent quality objective concentrations in 1957. These objectives were expanded in 1978 to include trace metal concentrations in cooling water. Oil and grease, phenols, suspended solids, ammonia-nitrogen, and COD are the process effluent pollutants covered. Objective limits were also issued for chromium, copper, nickel, lead, and zinc in cooling water. The 96-hour static test was developed by the province as a standard fish bioassay. The 96-hour flow-through test was not used because of the impracticality of transporting large volumes of effluents.

As an alternative to direct discharge, a refinery may discharge to a municipal treatment plant. Pollutant concentrations in the effluent must meet the limits set by the municipality's Sewer Use Bylaw. Any exceedence of these limits is subject to surcharge and review by the municipality as to the compatibility of the effluent with the municipal treatment system. In most cases, this effluent receives three stages of treatment at the municipal plant.

IN THE UNITED STATES

The 1972 and subsequent 1977 amendments to the FWPCA require all industrial existing dischargers to achieve specific levels of pollutant control in a two-step process: 1) by July 1, 1977, achieve BPT for all pollutants, and 2) by July 1, 1984, provide BCT for conventional pollutants such as BOD₅ and TSS, and BAT for all toxic pollutants referred to in Appendix VI of this report and also for nonconventional pollutants.

U.S. EPA promulgated effluent limitations guidelines for BPT, BAT, New Source Performance Standards (NSPS), and Pretreatment Standards for New Sources (PSNS) for the Petroleum Refining point source category on May 9, 1974. These regulations divided the petroleum refining industry, as defined by the Bureau of Census Standard Industrial Classification (SIC) 2911, into five subcategories: A-Topping, B-Cracking, C-Petrochemical, D-Lube, and E-Integrated. Subsequently, the BPT, BAT, and NSPS regulations were challenged in the courts. The court upheld the BPT and NSPS limitations, but returned the BAT limitations to the Agency for further consideration. After the regulations were published, comments were received criticizing certain aspects of the regulations. As a result of these comments, amendments to the BPT and NSPS regulations were issued on May 20, 1975. Concluding this first round of regulations was promulgation of interim final Pretreatment Standards for Existing Sources (PSES) on March 23, 1977. BPT standards for the five subcategories of the industry appear in Appendix VII.

The pretreatment standards for existing sources in all refinery subcategories discharging to municipal sewerage systems limit the ammonia, and oil and grease concentrations to a daily maximum of 100 mg/L. In addition pollutants shall not:

- create a fire or explosion hazard;
- cause corrosive structural damage to treatment works, and in no case have a pH lower than 5.0;
- be solid or viscous in amounts which would cause obstruction to the flow in sewers, or other interference with proper operation; and
- be released in such volume or strength as to cause interference with proper operation.

The General Pretreatment Standards promulgated by U.S. EPA in 1981 for all users of municipal systems include the above requirements as well as a temperature requirement. These standards define any of the above characteristics as "prohibited discharges" and also establish the basic mechanisms for developing and operating a pretreatment program at the federal, state and local levels. At this time, there are no specific federal pretreatment requirements for discharges from re-refineries. Municipalities may enact local ordinances regulating substances which may be found in any discharge to their system including discharges from refineries and re-refineries.

Following the amendments to the Clean Water Act in December 1977, the Agency undertook to restudy this industry with the goal of developing effluent limitations aimed principally at controlling toxic pollutants. Because information on the discharge levels of many of the toxic pollutants shown in Appendix VI was limited or unknown, investigations were initiated for all of the primary industries, including petroleum refining. These investigations consisted of initial industrial surveys, wastewater sample and analysis, and treatment technology evaluations.

INDUSTRY SURVEYS

The initial effort in the investigation involved the review and evaluation of existing industrywide data on such factors as refinery characteristics,

production capacities, wastewater handling techniques, and wastewater characteristics. Then the Agency supplemented the existing data base by sending a comprehensive questionnaire to all refineries throughout the United States and its territorial possessions. The information gathered from the questionnaire survey included number of plants, their size, geographic location, manufacturing processes, wastewater generation, treatment practices, and discharge methods. In addition, information on the use or generation of selected toxic pollutants and effectiveness of toxics removal was also requested. The information from the survey was used in part to aid in the selection of plants for the next phase of the investigation, the wastewater sampling and analysis program.

SAMPLING AND ANALYSIS PROGRAM

Sampling visits were made to each of 23 refineries for three consecutive days of plant operation. Samples were taken before and after biological treatment. Intake waters were also sampled to determine the presence of toxic pollutants before contamination by refining processes. The plants selected were representative of the manufacturing processes, the prevalent mix of production among plants, and the current treatment technology in the industry. Seventeen plants were direct dischargers and six were indirect dischargers.

The analysis for priority pollutants were performed according to groups of chemicals and associated analytical schemes. Organic toxic pollutants included volatile (purgeable), base-neutral and acid (extractable) pollutants, total phenols, and pesticides. Inorganic toxic pollutants included heavy metals, cyanide, and asbestos. In addition, analyses were conducted for conventional pollutants (BOD₅, TSS, pH, and oil and grease), and nonconventional pollutants (TOC, sulfide, and COD).

TREATMENT TECHNOLOGY EVALUATION

Three major efforts were undertaken to identify and evaluate available control and treatment technologies. A literature search was carried out to compile information on advances being made by the industry relative to wastewater handling and disposal. A review of the responses to the industry surveys were performed to determine the status of the industry with regard to in-plant source control and end-of-pipe treatment operations. Visits to selected petroleum refineries were conducted to identify and review the sources of wastewater production and wastewater flow reduction practices, reuse, and in-plant and end-of-pipe treatment operations.

These studies established a range of control and treatment technologies available to the petroleum refining industry. Results were used as a basis for estimating compliance costs for the various technology options. Economic and other non-water quality impacts were also assessed. Alternatives considered by the Agency in developing proposed effluent limitations guidelines for direct and indirect discharge sources included reuse and recycle of wastewaters resulting in reduction of total effluent flow; powdered activated carbon enhancement to improve removal capabilities of biological treatment; granular activated carbon treatment after BPT treatment; metals

removal by pH adjustment, precipitation, and clarification; biological pretreatment; and vapor compression distillation with flash drying.

Following proposal of effluent guidelines in December 1979, three additional studies were conducted to further evaluate BAT and resolve issues raised during the comment period. The studies consisted of the evaluation of flow reduction techniques and their associated costs at 15 refineries, a survey of effluent data from 50 refineries, and a long-term sampling and analysis program at two refineries.

The results of the data-gathering efforts described herein will be used by EPA in its decision-making process to establish effluent limitations guidelines and standards for the petroleum refining industry. Final regulations for BAT, BCT, NSPS, PSES, and PSNS are scheduled for promulgation before the end of 1982.

Analytical Protocols

Analytical protocols used in the United States were specified by U.S. EPA in a regulation issued in 1973 and amended in 1976. The "Test Procedures for the Analysis of Pollutants," contains standard test methods for 115 pollutants, including those of concern in refinery effluents (BOD₅, COD, TSS, oil and grease, total phenols, ammonia-nitrogen, sulphide, and chromium). Other approved procedures which may be used in place of the U.S. EPA protocols are listed in Appendix VIII [1].

In the preparation of the BAT guidelines, the primary method used to screen and verify the volatiles, base-neutral, and acid organics was gas chromatography with confirmation and quantification of all priority pollutants by mass spectrometry (GC/MS). Total phenols were analyzed by the 4-AAP method. GC was employed for analysis of pesticides with limited MS confirmation. Toxic heavy metals were analyzed by atomic adsorption spectrometry (AAS), with flame or graphite furnace atomization following appropriate digestion of the sample. Duplicate samples were analyzed using plasma emission spectrometry after appropriate digestion. Samples were analyzed for cyanides by a colorimetric method, with sulfide previously removed by distillation. Analysis for asbestos was accomplished by microscopy and fiber presence reported as chrysotile fiber count. Analyses for conventional pollutants (BOD₅, TSS, pH, and oil, and grease) and nonconventional pollutants (TOC and COD) were accomplished by using "Methods for Chemical Analysis of Water and Wastes" (EPA 625/6-74-003) and amendments.

Approved protocols must be used by dischargers regulated under NPDES permits. The state governments are required by law to have structured self-monitoring and quality assurance programs which incorporate U.S. EPA approved analytical methods.

The Canadian Federal Regulations and Guidelines specify APHA-AWWA-WPCF, 13th Edition, test methods for the petroleum refining industry, for oil and grease, TSS, volatile suspended solids, total phenols, sulphides, and ammonia-nitrogen (see Appendix VIII [2]).

Discussion between PACE and EPS concerning the updating of analytical protocols are in progress and may ultimately result in a revision to the Regulations and Guidelines.

The provincial laboratories, in analyzing refinery effluents for the purposes of Ontario's Quality Assurance Program, utilize modified APHA-AWWA-WPCF, 13th and 14th Editions, methods with greater automation. These methods are presented in the "Outlines of Analytical Methods" (1981).

When comparing various standard methods, analytical chemists are concerned with precision and accuracy. The precision, or standard deviation of test results, is very similar for the various standard methods. The accuracy of a given method depends on the source of the effluent, the effect of background interferences, the quality of reference materials used, the capability of the method, and the proper use of the method. Although the accuracy of the approved analytical protocols used in Canada and the United States will vary, the Task Force concludes that this variability is not paramount when comparing jurisdictional data.

Self-Monitoring and Federal/State/Provincial Inspection Programs

Industries which discharge pollutants directly into the "waters of the United States" are required by the conditions of their NPDES permits to self-monitor to assure compliance with permit limitations for designated parameters. The permit holder must monitor at the frequencies shown in the permit, using an indicated sample type. The analyses must be conducted according to U.S. EPA approved test procedures. Records must include: the date, the exact place and time of sampling or measurements, the date analyses were performed, the individual who performed the analyses, and the analytical techniques or methods used. If the permit holder monitors any pollutant more frequently than required by the permit, these results must also be reported.

The monitoring results are reported on special forms and sent to the permit issuing authority at specified intervals. All records and information resulting from the required monitoring activities must be retained by the permit holder for a minimum of three years.

During 1980, U.S. EPA conducted a national Discharge Monitoring Report - Quality Assurance (DMR-Q/A) sampling program. Through this program, several thousand holders of NPDES permits were sent standard samples which were to be analyzed and the results reported for comparison with the "true" values. To account for recognized analytical precision and accuracy, a reported value was considered acceptable if within a given range of the true value.

A statistical breakdown of the results reported by the petroleum refineries in the Great Lakes Basin which participated in this program is given in Table 2. As a first round effort, this program is generally indicative of the analytical performance of the refineries in the Great Lakes Basin. NPDES states were encouraged to use this information to improve their inspection programs by placing a greater emphasis on reviewing the quality assurance aspects of a facility's self-monitoring program. Sampling and testing problems identified during these inspections are brought to the attention of the permittee with a requirement that corrective actions be taken accordingly.

A second round DMR-Q/A program, with improved instructions, is being undertaken in 1982. The results are not expected until early 1983.

A permit holder's facilities can be inspected by either the U.S. EPA or the state to determine compliance with the required limitations and to assure that the required monitoring protocols are used. Below are summaries of Inspection and Quality Assurance (Q/A) programs implemented by the U.S. EPA and the states:

TABLE 2. RESULTS OF DISCHARGE MONITORING REPORT - QUALITY
ASSURANCE SAMPLING PROGRAM FOR GREAT LAKES BASIN PETROLEUM REFINERIES

Parameter	Results	
	Not Acceptable	Acceptable
Cu	1	0
NH ₃	4	2
Total P	1	2
COD	4	2
BOD ₅	1	5
Cr	1	3
Oil and Grease	2	3
Pb	0	1
Zn	0	1
pH	0	6
TSS	0	6
TOC	0	2
TOTAL	14	33

Number of refineries = 6.

Total number of parameters tested = 47.

Total number of "not acceptable" results = 14 or 30%.

1. Compliance Evaluation Inspections (CEI) are non-sampling inspections. These surveys include a review of any of the following:
 - Progress with the compliance schedule
 - Laboratory procedures
 - Plant operating procedures
 - Sampling procedures
 - Reporting procedures
 - Operator certification
 - Other permit-related activity
2. Compliance Sampling Inspections (CSI) are surveys designed to be detailed plant inspections, which include the sampling of the permit holder's discharge and any of the other activities under the CEI class.
3. Performance Audit Inspections (PAI) evaluate the permit holder's sampling techniques, analytical procedures, quality control procedures, Discharge Monitoring Report (DMR) data, and compliance schedules.
4. DMR-Q/A Evaluations are designed to improve the quality of DMR data. General quality control practices are reviewed to ascertain the causes of unreliable or unacceptable data. Part of this evaluation may include requiring the discharger to analyze samples of known values. Where the reported values indicate poor quality control practices, follow-up actions are initiated.

INDIANA

Self-monitoring began in Indiana with a voluntary program in 1968 of major dischargers submitting monthly operation reports consisting of state predetermined parameters.

When accurate flow metering was established, many industries installed continuous sampling instruments which gave daily composite samples which could be analyzed to reflect more accurately loadings to the stream. By 1972 the NPDES permit program required effluent sampling of all discharges. Indiana promulgated a Regulation (330 IAC 3-3-23) which provides for the monitoring, recording, and reporting of any discharge regulated by an NPDES permit. Dischargers are required to retain records of monitoring for a period of three years. This period of retention shall be extended during periods of litigation.

Indiana maintains Q/A documents which outline everything from field procedures and chain of custody of samples collected to laboratory methodology. The state has three Q/A coordinators: one for field activities, one for water laboratory activities, and one for fish and organics analysis laboratory activities. Each coordinator reports to a Q/A officer, who is basically responsible for the Q/A program.

WISCONSIN

The Wisconsin DNR requires discharge monitoring reports of its dischargers and its six district offices follow up any violations through compliance sampling and/or evaluation inspections in the field. These inspections include the discharger's laboratory and can lead to enforcement action if laboratory procedures are found to be poor.

OHIO

In Ohio, NPDES permits require all dischargers to file Monthly Operating Reports (MOR).

Upon request, the Ohio EPA inspects a permittee's laboratory and evaluates its quality assurance program.

NEW YORK

In New York, permitted facilities are required to submit discharge monitoring reports (DMRs) to the state regional office, the central office in Albany, and the local health department. Quality assurance and laboratory practices are reviewed at a particular facility at the time the state performs its scheduled inspection. Under certain circumstances (e.g. special parameter testing), the results of spiked or duplicate samples must also be submitted to the state.

Within the past year the state has initiated a program using the 96-hour fish bioassay to test discharges from both industries and municipalities.

MICHIGAN

Michigan, for the past 30 years, has conducted industrial wastewater surveys for determining compliance with its rules and regulations. The first surveys consisted primarily of grab sampling and limited flow measurements of a discharge. This has now evolved into very sophisticated sampling surveys utilizing continuous samplers, automatic flow recording, and sensitive on-site biological monitoring.

Michigan also participates in the U.S. EPA programs of self-monitoring requirements, compliance evaluation inspections, compliance sampling inspections, performance audit inspections, and the quality assurance programs. In addition, Michigan has a Field Operations staff throughout the state to perform unannounced visits for the purpose of collecting water samples and evaluating an industry's compliance with both federal and state requirements.

ONTARIO

In 1970 the petroleum refineries began self-monitoring by submitting an annual report on their effluent quality and the status of their effluent improvement program. The effluent quality information was verified by an annual survey of the Ontario Water Resources Commission. Five effluent parameters were monitored: phenols, pH, suspended solids, BODs, and oil and grease.

As effluent treatment systems were expanded, flow measurement was improved, and the installation of continuous automatic instruments began; for example, pH meters. Composite effluent samplers were also installed. By February 1974, the refiners were sending in monthly reports in accordance with Federal guidelines to the provincial agency. Flow rates and pH are monitored on a continuous basis. Flow proportioned 24-hour composite samples are collected at least three times a week and analyzed for oil and grease,

phenols, sulphide, ammonia-nitrogen, and total suspended matter. The results are reported monthly to the Ontario Ministry of the Environment. For monitoring purposes, the refiner also performs a monthly 24-hour static bioassay on liquid effluent and once-through cooling water. The monthly data is evaluated at the Ministry's District Office nearest the refinery. Effluent concentration trends and daily averages for the month are checked against requirements.

In 1980 the development of the Industrial Monitoring Information System, a new automatic data system, began. The data bank includes information on effluents, air emissions, and solid wastes from industrial point sources. The vast bulk of this data will be self-monitoring company information. By mid-1982 all the Regional Offices will have the ability to input and retrieve information from the central Ontario computer at Downsview (Metropolitan Toronto) through live terminals. This capability will be extended to the various District Offices over a five year-period. Fixed data about each point source are being entered. By year end, data from the monthly reports should be entered.

The self-monitoring monthly reports consists of effluent loadings in both concentration (milligrams/litre) and weight (kilograms per day) units. Since federal pollutant allowables are related to the actual crude rate, some report their discharges per thousand barrels of processed crude oil. Excursions above the provincial concentration and/or federal limits are investigated.

These requirements are obligatory for new refineries which fall under the Refinery Effluent Regulations. The requirements are not legally binding on existing refineries (processing crude prior to November 1, 1973), however, all existing refineries have cooperated fully in the self-monitoring program since 1973. Some existing refineries are no longer required to report sulphide where the concentration in the effluent has remained consistently undetectable.

In Ontario, the provincial government has the responsibility for quality assurance. The analytical needs for the various Ministry of the Environment programs are met by its Control and three Regional Laboratories. The Laboratories Services group exerts a continuous effort to maintain its own quality assurance standards. Ontario refineries are inspected regularly by provincial officials. During the inspection, effluent audit samples are taken, plant operating records are reviewed, the performance of the treatment system is observed, and the results of past performance are discussed with the treatment system operators and with refinery management. The effluent samples are split and analysis results are compared. Any significant differences are investigated and resolved. Environment Canada provides a contractor who performs annual 96-hour static toxicity tests on refinery effluents using provincial bioassay facilities.

SUMMARY

Self-monitoring programs for the petroleum refinery industry are established in response to jurisdictional requirements. Their purpose is to identify non-compliance situations quickly and to uncover serious problems. It is the opinion of the Task Force that this purpose is adequately served by the existing self-monitoring programs.

Discharge Trends

At the end of 1981, 15 refineries were discharging wastewater directly to the Great Lakes Basin. During the period of 1972-1981, a number of refineries closed and others commenced production. In Canada (Ontario), the volume of crude processed has increased by more than 50%. In the United States, crude production by refineries discharging directly to the Great Lakes has decreased by 34%. The discharge trends, as a result, are presented as both loading per day and loading per 1000 barrels of crude processed (Table 3).

Pollutant loading from the refining industry interpreted on a production basis is more indicative of true pollutant reductions by the industry due to improvements in wastewater treatment and modified water usage during the period. The total pollutant loadings in kg/day indicate the change in the magnitude of waste discharges by this industrial sector.

Although a complete set of data was not available for all jurisdictions, the overall trend appears to have been a decreased average daily loading and a decreased loading per unit of production. The sharp decreases in pollutant loading in the early seventies appear to be tapering off. The major reductions occurred as a result of the retrofitting of wastewater treatment technology in the first half of the last decade, and the starting up of new refineries which incorporated this technology in their design.

In Canada, the following average daily (and per 1,000 barrels of production) reductions have been achieved since 1976: total suspended solids 70% (78%), phenols 46% (50%), ammonia 65% (74%), and oil and grease 75% (81%).

In the United States, the following average daily (and per 1,000 barrels of production) reductions have been achieved since 1976: total suspended solids 83% (74%), phenols 96% (94%), ammonia 83% (72%), and oil and grease 89% (85%).

Overall, the following reductions in loading of pollutants to the Great Lakes Basin have been achieved since 1976: total suspended solids 77% (73%), phenols 88% (88%), ammonia 78% (72%), and oil and grease 83% (81%).

These trends are expected to continue in the future as use of closed loop cooling and air cooling replace once-through water cooling and recycle and re-use of treated effluent become more common. The projected minor decreases in production will also marginally reduce total discharges, however, this is not anticipated to have a major impact.

Another factor in the achievement of continued reductions is the availability of qualified, well-trained operators of wastewater treatment facilities. While much of an effluent treatment system is automated, a knowledgeable operator is needed to monitor and make system adjustments.

TABLE 3. SUMMARY OF DISCHARGE TRENDS OF POLLUTANTS FROM PETROLEUM REFINERIES DISCHARGING DIRECTLY TO THE GREAT LAKES

Jurisdiction	Year	No. of Plants	Flow L ³ /Day	Oil and Grease kg/Day	TSS kg/Day	NH ₃ -N kg/Day	Phenols kg/Day	BOD ₅ kg/Day	COD kg/Day	Cyanide kg/Day	Sulfides kg/Day	Chromium kg/Day	Tot-P kg/Day	Production 1000 bbls/Day
MICHIGAN	72-74	5	87,444	870	3,483	3,955	8	N/A	N/A	N/A	N/A	N/A	N/A	13.0(81.5)
	76-77	4 ^a	9,154	18	113	34	1.8	102.4	520	N/A	7.1	N/A	2.0	8.7(54.8)
	80	3 ^b	7,665	18.6	143.3	6.9	.11	24.2	375	N/A	.12	N/A	N/A	9.1(57.5)
	81	3 ^c	7,684	26.4	163.7	16.9	1.08	97.1	604	N/A	.10	N/A	.5	9.1(57.5)
OHIO	72-74	4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	76-77	4	340,024	513	2,331	1,064	12.00	1,780	7,443	3.6	N/A	10.8	18.9	77.4(487)
	80	3 ^d	83,656	121	959	282	3.01	758	4,869	1.0	N/A	3.6	13.6	57.3(360)
	81	3	69,046	194	938	237	2.46	1,124	5,538	1.3	N/A	3.3	18.6	49.3(310)
INDIANA	72-74	4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	76-77	2 ^d	11,730	2,253	4,696	527	67.2	N/A	N/A	N/A	N/A	N/A	N/A	74.4(468)
	80	2	64,730	173	259	44.6	1.04	216	2,930	N/A	1.72	1.8	N/A	63.3(398)
	81	2 ^e	56,900	118	189	40.8	0.78	184	2,340	N/A	1.00	2.6	N/A	63.3(398)
WISCONSIN	72-74	1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	6.0(38)
	76-77	1	N/A	9.0	22.0	19.0	0.06	N/A	N/A	N/A	N/A	N/A	N/A	6.0(38)
	80	1	901	6.6	15.9	10.2	0.03	24.9	146	N/A	.02	.02	N/A	3.0(18)
	81	1	1,022	8.1	21.8	13.2	0.05	24.0	141	N/A	.03	.02	N/A	3.2(20)
NEW YORK	72-74	3	N/A	525	N/A	846	42	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	76-77	2 ^a	N/A	277	583	474	25.5	N/A	N/A	N/A	N/A	N/A	N/A	16.7(106)
	80	0 ^b	0	-	-	-	-	-	-	-	-	-	-	0
	81	0	0	-	-	-	-	-	-	-	-	-	-	0
MINNESOTA	72-74	1	N/A	6	16	10	1.0	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	76-77	1	N/A	6	18	3	0.09	N/A	N/A	N/A	N/A	N/A	N/A	2.9(18)
	80	0 ^a	0	-	-	-	-	-	-	-	-	-	-	0
	81	0	0	-	-	-	-	-	-	-	-	-	-	0

TABLE 3 (continued)

Jurisdiction	Year	No. of Plants	Oil and Grease kg/Day (kg/1000 bbls)	TSS kg/Day (kg/1000 bbls)	NH ₃ N kg/Day (kg/1000 bbls)	Phenols kg/Day (kg/1000 bbls)	Production 1000 M ³ /Day (1,000 bbls/Day)
U. S. TOTALS	76-77	15	3,076 (2.6)	7,763 (6.6)	2,121 (1.8)	106.7 (.09)	186 (1,171)
	80	9	319 (0.4)	1,377 (1.6)	341 (0.4)	4.2 (.005)	133 (835)
	81	9	346 (0.4)	1,313 (1.7)	358 (0.5)	4.3 (.005)	125 (786)
ONTARIO	72-74	7	3,279 (8.1)	13,257 (32.9)	1,775 (4.4)	38 (0.09)	64.0 (403)
	76-77	8 ^f	2,056 (4.3)	7,019 (14.7)	893 (1.9)	18.8 (0.04)	75.7 (476)
	80	8	1,242 (1.9)	2,458 (3.8)	410 (0.6)	17.2 (0.03)	103 (646)
	81	8	514 (0.8)	2,074 (3.3)	313 (0.5)	10.2 (0.02)	101 (633)
GREAT LAKES BASIN TOTALS	76-77	23	5,132 (3.1)	14,782 (9.0)	3,014 (1.8)	125.5 (0.08)	262 (1,647)
	80	17	1,561 (1.1)	3,835 (2.6)	754 (0.5)	21.4 (0.01)	235 (1,481)
	81	17 ^g	859 (0.6)	3,387 (2.4)	671 (0.5)	14.5 (0.01)	226 (1,419)

^aOne refinery permanently closed.^bOne refinery process water to POTW.^cOne refinery temporarily closed.^dTwo refineries permanently closed.^eOne refinery closed, one refinery process water to POTW.^fOne refinery closed, two new refineries built.^gOnly 15 plants are currently operating (as of November, 1982).

N/A = Not Available

In the United States, the laws of many states require that a certified operator be in responsible charge of wastewater treatment systems. Indiana, Michigan, and Wisconsin have specific requirements for the certification of these operators. For instance, in Indiana and Michigan operators must pass a written examination for different levels of competency. In Canada, there is no federal or provincial requirement for a certified operator.

These operator certification programs promote a high degree of awareness among operators since habitual effluent violations, poor plant operation or falsification of reports could lead to revocation of their certification. This recognition of responsibility on the operator's part can often lead to an extra effort to produce the best quality effluent that may well be an order of magnitude better than the permit requirements.

The certification requirements have led to an improvement in overall wastewater treatment and a consistent effluent quality. Furthermore, this program has spawned a number of educational seminars and workshops where operators can get together, share common problems, work out solutions and obtain additional training and education.

The Ontario Ministry of the Environment encourages the operators of municipal sewage treatment plants to be trained by conducting several training courses each year. Operators run a small waste treatment plant at Brampton, Ontario as part of the training course. Industry has sent operators to these training courses.

Compliance

Compliance is interpreted in terms of the environmental requirements set by a regulatory agency. These requirements may be rigorous legal limits which must not be exceeded or objectives which are desirable levels achieved through cooperative effort with the industry. Legal limits are the values prescribed in discharge permits under the U.S. National Pollutant Discharge Elimination System (for new and existing refineries) based on Best Practicable Control Technology (BPT) effluent guidelines limitations issued by the U.S. EPA. Legal limits based on BPT are also prescribed by Environment Canada's Petroleum Refinery Effluent Regulations (for new refineries). In Canada, reduction in the discharge of pollutants is also brought about by setting voluntary guidelines or target limits based on similar treatment technology. Such limits are published in Environment Canada's Petroleum Refining Guidelines (existing refineries) and Ontario's Liquid Effluent Guidelines for the Petroleum Refinery Industry (new and existing refineries).

Thus an interpretation of compliance goes beyond a numerical comparison of actual versus legal or target levels. For purposes of this report, a refinery that is meeting the permitted loading limit for all regulated parameters on a monthly average basis is considered to be in compliance. Table 4 provides this information for refineries in the Great Lakes Basin. A description of any remedial actions being taken to achieve compliance at individual refineries as well as a description of compliance problems at these refineries follows.

ONTARIO

The petroleum refineries in Ontario must comply with the more stringent of three possible requirements. These requirements may be either limits based on the quality of the receiving waterbody, federal allowances (legal or objectives) or provincial concentration objectives. Under the Canada-Ontario Accord for the Enhancement of Great Lakes Water Quality, Ontario adopts the federal limits as the minimum requirement where local considerations or provincial objectives are not limiting. For these reasons, the compliance limits may be either daily or monthly maximum concentrations or monthly average loadings. In 1980, the monthly 24-hour static fish test was consistently passed by the refineries with the exception of British Petroleum, Oakville; Shell, Oakville; and Gulf, Mississauga. The provincial 96-hour static fish test was passed for 1980 and 1981 by all refineries.

The two newest refineries, Texaco and Petrosar, were consistently below the federal legal allowances. However, Petrosar tended to exceed Ontario's total suspended solids concentration objective of 15 mg/L. The suspended solids problem is caused by shearing action when the aerators are at low speed. Petrosar is considering several alternatives to correct this problem. Petrosar exceeded the phenolics concentration objective by 0.05 mg/L. At present, these exceedances are considered insignificant because the load is small (0.3 kg/day) and there are few days when the objective is exceeded.

TABLE 4. PETROLEUM REFINERY COMPLIANCE SUMMARY FOR 1980

Refinery		Exceedences of Compliance Limits*				
		Oil & Grease	Suspended Solids	Phenols	Sulphide	Ammonia
ONTARIO						
BP Oakville	No. Limit kg/day (lbs/day) No. of Exceedences	114 (252) 0	274 (605) 0	.02 mg/L** 3	3.8 (8.4) 0	95 (210) 0
Gulf*** Mississauga	No. Limit kg/day (lbs/day) No. of Exceedences	10 mg/L** 4	15 mg/L** 8	.02 mg/L** 15	6.7 (14.8) 1	177 (390) 0
Imperial Sarnia	No. Limit kg/day (lbs/day) No. of Exceedences	329 (726) 1	792 (1,742) 0	32.9 (72.6) 0	2.2 (4.8) 0	275 (605) 0
Petrosar Corunna	No. Limit kg/day (lbs/day) No. of Exceedences	136 (300) 0	15 mg/L** 5	.02 mg/L** 2	45 (100) 0	163 (360) 0
Shell Corunna	No. Limit kg/day (lbs/day) No. of Exceedences	198 (437) 5	477 (1,050) 5	19.8 (43.7) 0	6.6 (14.5) 0	166 (366) 0
Shell Oakville	No. Limit kg/day (lbs/day) No. of Exceedences	125 (276) 0	301 (662) 0	12.5 (27.6) 0	4.2 (9.2) 0	104 (230) 3
Suncor Sarnia	No. Limit kg/day (lbs/day) No. of Exceedences	169 (371) 0	405 (890) 1	16.9 (37.1) 0	5.6 (12.3) 0	159 (349) 1
Texaco Nanticoke	No. Limit kg/day (lbs/day) No. of Exceedences	137 (302) 0	329 (725) 0	13.7 (30.2) 0	4.6 (10.1) 0	165 (363) 0

*BOD₅, COD, Chromium and Phosphorus are not limited in Ontario.

**Daily maximum concentration limit; violation number represents typical number of days in a month that limit was exceeded.

***Gulf also had 8 monthly limit violations of oil and grease in stormwater.

Exceedences of Compliance Limits

Refinery	Exceedences of Compliance Limits								Total Phos.	
	Oil & Grease	Suspended Solids	Phenols	Sulphide	Ammonia	POD ₅	COD	Chromium (Hexa.)		
WISCONSIN										
Murphy Oil Superior	P.O. Limit kg/day (lbs/day) No. of Months Exceeded	37.0 (81.4) 0	102 (224) 0	.83 (1.83) 0	.67 (1.46) 0	57.9 (127.5) 0	111 (245) 0	£88 (1955) 0	.2E* (.61) 0	** *
MICHIGAN										
Lakeside Kalamazoo	P.O. Limit kg/day (lbs/day) No. of Months Exceeded	10 mg/L* 8	4.1 (9) 1	0.3 mg/L* 0	0.05 mg/L 0	1.4 (3.0) 0	5.4 (12) 0	15.9 (35) 0	** 0	** 0
Osceola West Branch	P.O. Limit kg/day (lbs/day) No. of Months Exceeded	10 mg/L* 0	9.5 (21) 0	0.1 (0.2) 0	0.1 (1.8) 1	1.5 (3.3) 1	14.1 (31) 0	72.6 (160) 1	** 0	** 0
Total										
Petroleum Alma	P.O. Limit kg/day (lbs/day) No. of Months Exceeded	10 mg/L* 0	79.4 (175) 0	0.8 (1.7) 0	0.6 (1.4) 0	66.3 (146) 0	72.6 (160) 3	849 (1,870) 0	** 0	** 0
INDIANA										
Arco Whiting	P.O. Limit kg/day (lbs/day) No. of Months Exceeded	780 (1,720) 0	2,065 (4,597) 2	15.9 (35) 0	13.6 (30) 0	470 (1,036) 0	2,370 (5,225) 0	17,185 (37,886) 1	2.7 (6.0) 0	** 0
OHIO										
Standard Oil Lima	P.O. Limit kg/day (lbs/day) No. of Months Exceeded	159* (371) 0	603 (1,329) 0	1.14 (2.51) 0	3.86 (8.51) 0	370 (816) 0	359 (751) 8	2,273 (5,011) 0	.44* (.97) 0	19.1 (42.1) 0
Standard Oil Toledo										
Standard Oil Toledo	P.O. Limit kg/day (lbs/day) No. of Months Exceeded	206* (454) 0	559* (1,232) 1	3.95* (8.71) 0	3.18* (7.01) 0	329* (725) 4	700* (1,540) 0	4,930* (10,870) 0	.614* (1.35) 0	** 0
Sun Oil Toledo	P.O. Limit kg/day (lbs/day) No. of Months Exceeded	146 (322) 0	300 (661) 0	1.50 (3.31) 0	2.52 (5.56) 0	N/A 0	305 (672) 0	1,820 (4,010) 0	.955 (2.11) 0	** 0
*Monthly Maximum Limit **Not Limited										

British Petroleum was consistently below the federal limits. However, Ontario's phenolics concentration objective is usually exceeded by 0.01 mg/L. This is not considered significant because the load is small (0.1 kg/day) and there are few days when the objective is exceeded. Occasionally during the winter, the ammonia concentration peaks as high as 30 mg/L. Fish die-offs in 1960 appears to have been associated with these high ammonia levels.

Shell at Oakville usually does not exceed the provincial concentration objectives. However, in 1980 the refinery did exceed the concentration objectives for total suspended solids and ammonia by 4 mg/L and 8 mg/L respectively. The federal allowance for ammonia was exceeded for three months in 1980, because desalter upsets caused by surges in slop injection were not adequately handled by the effluent treatment system. This has been corrected by modifying the slop handling system. For the first half of 1981, the ammonia concentration in the effluent was in the 4 mg/L range.

In 1980, the effluent from Esso Petroleum (Imperial Oil) had an average concentration of 1 mg/L for oil and grease, however, the federal limit was exceeded for one month. In 1981 the average concentration was further reduced to 0.8 mg/L. It should be noted that this effluent includes some loadings from petrochemical processes. The Ministry of the Environment is concerned about the phenolic loadings in the effluent.

Since Gulf Oil significantly exceeded the provincial limits for total suspended solids, phenolics, and oil and grease in 1978-79, the Ministry of the Environment required improvements to the effluent treatment system. The API separators were modified and a new activated sludge unit was constructed. These changes have been completed and the new system should be on stream by October 1982. In 1980 prior to these treatment system modifications, the federal oil and grease and sulphide objectives were exceeded for three months and one month, respectively. The loadings of oil and grease and suspended solids were also exceeded in stormwater which is discharged separately. The oil and grease limit was exceeded eight months, while the suspended solids limit was exceeded two months. Gulf Oil discharges a small volume of high-strength phenolic wastes to a municipal sewer. Since the phenol concentration exceeds the municipality's Sewer Use Bylaw limit, the refinery must pay a surcharge.

Suncor usually meets provincial concentration objectives, but did exceed the federal allowable objectives for total suspended solids and ammonia for one month each in 1980.

The Shell Canada, Corunna effluent also contains the loading from a petrochemical plant. In 1980 the refinery exceeded the phenolics concentration objective. Two changes were made in the treatment system to correct this by mid-summer of 1981. First, the control of caustic addition to the ammonia and phenol stripper was improved. Second, mixing in the effluent equalizer basin was improved. As a result, the average concentration of phenol decreased from 25 µg/L to 1 µg/L for the years 1980 and 1981, respectively. Ontario's concentration objectives for total suspended solids and oil and grease were consistently exceeded by the refinery in 1980. The federal allowances were exceeded for five months for each of these parameters. A new flocculent is being added to the clarifier at the biological oxidation unit. As a result, concentrations for these two pollutants in 1981 were 70% lower than in 1980.

OHIO

Major efforts to comply with effluent limitations and water quality standards are currently underway at two Ohio refineries.

Standard Oil Company of Ohio (SOHIO) has consented to relocate the thermal discharge at their Toledo Refinery from the mouth of Otter Creek to a location out in Maumee Bay. The relocation of this discharge will remove a thermal barrier which had previously impeded fish movement up Otter Creek to adjacent wetland nursery areas.

The SOHIO Lima Refinery is installing a completely new wastewater treatment system which will correct BOD₅, COD and TSS problems and will facilitate compliance with expected BAT limits.

INDIANA

Indiana has one currently operational refinery, Amoco Oil at Whiting. Compliance with NPDES permit limitations based on federal effluent treatment guidelines and water quality standards has required Amoco to construct aeration facilities, clarifiers, and multi-media gravity filters which are now operational.

WISCONSIN

The one Wisconsin refinery, Murphy Oil Corporation at Superior, is in compliance with its current NPDES permit. This permit required improved flow monitoring equipment which the refinery has installed.

NEW YORK

The Ashland Oil Refinery near Buffalo has discharged its process wastewaters to a municipal treatment system for many years. The only regulated direct discharges are for cooling and storm water runoff. During the discharge year, February 1980 through January 1981, several minor pH excursions occurred along with one oil and grease (storm runoff) and two total organic carbon (cooling water) permit violations. A new permit, issued in early 1982, added iron and lead concentration limitations to the storm water runoff outfalls. Inclusion of these limitations has been contested by the company. Additional monitoring is underway to determine the levels of iron and lead from these discharge points. After the summer of 1982, the refinery portion of this facility will be shut down leaving only the tank farm/storage area in operation. Runoff from these areas is required to be regulated.

MICHIGAN

As of December 1980, the three Michigan refineries discharging process wastewater into tributaries of the Great Lakes Basin were in compliance with the terms and conditions of their permits. These refineries were Total Petroleum, Alma; Lakeside Refining, Kalamazoo; and Osceola Refining, West Branch. Crystal Refining in Carson City, which discharges only cooling water, was also in compliance with its permit; the Dow Bay Refinery, in Bay City, was permanently shut down.

In 1981 and 1982, Total Petroleum experienced effluent violations for phenolics during the winter months (January to March). These noncompliances were due to excessively high phenol loadings entering their wastewater treatment system. During the cold weather, these phenolics could not be removed by the biological treatment process, resulting in effluent violations. The company has been put on notice by the Michigan Department of Natural Resources to prevent any further phenol violations.

In September 1981, Osceola Refining Company shut down its operations due to inadequate crude supply. As of November 1982, it is uncertain if and when the refinery will once again be in operation.

Since 1980, Crystal Refining Company has been discharging their process wastewater into the municipal sewage treatment system. This leaves Total Refining Company and Lakeside Refining Company as the only refineries in Michigan with process wastewater discharges to the surface waters. Most of Lakeside's process water has been diverted to the municipal treatment system.

Prior to 1978 Lakeside was experiencing oil and grease violations of the stormwater portions of their permit. During 1978 and 1979 new equipment was installed but due to startup and other operational problems Lakeside was not able to consistently meet the oil and grease limits until early 1981. Since 1981 the company has been in compliance with the oil and grease limits on their stormwater discharge.

SUMMARY

The Petroleum Refineries in the Great Lakes basin generally meet jurisdictional requirements. While 1980 is probably a typical year with regard to compliance, it should not be taken to be an indicator of future trends, nor used to make future projections. Gulf Oil, Mississauga, Sheli, Corunna, Standard Oil, Lima and Total Petroleum, Alma have all had serious problems in the past, but each refinery has recently made major efforts to improve their compliance situation. These efforts have included optimization and modernization of existing wastewater treatment facilities as well as efficient water management and process waste recycle.

Areas of Concern

The Great Lakes Water Quality Board* has identified specific areas and parameters of concern in the Great Lakes Basin. These are areas where a Great Lakes Water Quality Agreement Objective or a jurisdictional standard, criterion, or guideline has been exceeded. The Board further separated these areas into two classes:

1. Class "A" where impairment of beneficial uses is severe; and
2. Class "B" where uses may be impaired.

Table 5 lists the refineries discharging into the areas of concern and the jurisdictional responsibility for those areas. The Task Force has examined each of these areas and reported on remedial programs affecting the petroleum refinery industry in this Section.

TABLE 5.
PETROLEUM REFINERIES DISCHARGING TO AREAS OF CONCERN

Area	Refinery	Jurisdiction
<u>CLASS A</u>		
Grand Calumet River and Indiana Harbor Ship Canal	Amoco Oil, Whiting	Indiana
Saginaw River System and Saginaw Bay	Total Petroleum, Alma Osceola Refining, West Branch	Michigan
St. Clair River	Imperial Oil, Sarnia Petrosar, Corunna Shell Canada, Corunna Suncor, Sarnia	Ontario
Maumee River	Sohio, Lima Sohio, Toledo Sun, Toledo	Ohio
<u>CLASS B</u>		
St. Louis River	Murphy Oil, Superior	Wisconsin

*1981 Report on Great Lakes Water Quality, Appendix II

GRAND CALUMET RIVER AND INDIANA HARBOR SHIP CANAL

The following parameters have been identified for this area:

Sediment: Oil and Grease, Volatile Solids, Total Phosphorus, Iron, Chemical Oxygen Demand, Zinc, Lead, Chromium, and PCBs

Fish: None listed

Water: Copper, Iron, Mercury, Zinc, Ammonia, Phenol, Conductivity, Cyanide, and PCBs

For this area of concern there is only one refinery: Amoco Oil at Whiting. Of the above parameters, six have been identified in the discharge. They are oil and grease, volatile solids, COD, chromium, ammonia, and phenol.

Of the remaining parameters, none have been specifically identified in this refinery's discharge. Some of the parameters, however, may be present in concentrations similar to those found in the screening survey for the petroleum industry (Appendix IX).

The impact on this drainage basin is due to the combined effect of all dischargers in this area of concern and not primarily to the refinery. For example, Amoco was in compliance on a monthly average basis for phenol and ammonia in 1980 (Table 4). However, steel mills in the area discharge their wastewaters, which are high in phenolic compounds and ammonia, to the East Chicago sewerage system. This wastewater passes through the municipal treatment plant with little effective treatment.

REMEDIAL ACTION

The State of Indiana has proposed a Waste Load Allocation Study for this area of concern. This will update wasteload allocations made in this area in 1974 and will take into account new water quality standards, projected effluent flows for all dischargers, and seasonal differences in allowable wasteloads. Amoco's effluent will be considered in this study, especially its phenol and ammonia loading.

SAGINAW RIVER SYSTEM AND SAGINAW BAY

The following parameters are identified for this area:

Sediment: PBBs, PCBs

Fish: PCBs, Hexachlorobenzene, PBBs, Dioxin

Water: Total Dissolved Solids, Total Phosphorus

For this area of concern there are two refineries discharging into the watershed. Total Petroleum at Alma and Osceola Refinery at West Branch both discharge into tributaries of the Saginaw River System. Of the above parameters, only total dissolved solids and phosphorus have been consistently identified in the discharge. Neither of these parameters are presently regulated in the facilities' NPDES permits. The State of Michigan could require regulation if the need presents itself.

Presently total phosphorus concentrations in these discharges are less than 1 mg/L. Total dissolved solids concentrations at both facilities are often above 1000 mg/L. PCBs were found in the discharge from Total Petroleum in a 1981 survey by the State of Michigan at concentrations below 1 µg/L. PCBs have not been found in the discharge from Osceola Refinery Company.

Of the remaining parameters, none have been specifically tested for in either of the refineries discharge. It is doubtful that they would be present since these parameters are not commonly associated with the refinery industry.

REMEDIAL ACTION

The total phosphorus concentrations in the refinery effluent do not pose a significant input to the phosphorus problem in the area of concern. The total dissolved solid concentrations may be a contributor to keeping the area of concern above the IJC objective of 200 mg/L. There are many other discharges within the basin, plus numerous nonpoint sources that also contribute to the total dissolved solid loadings to the area of concern. Due to the complexity of this situation, it is impossible to single out the refineries as significant contributors to the problem without a wasteload allocation approach.

The source of PCBs in the discharge of Total Petroleum is currently being investigated by the State of Michigan. To date, the company has resampled their discharge and have not been able to detect PCBs in the wastewater.

ST. CLAIR RIVER

The following parameters were identified for this area:

Sediment:	PCBs, Organic Compounds, Mercury
Fish:	Mercury
Water:	Phenolics Compounds, Trace Organics

Nineteen major industrial sources discharge into the St. Clair River. These industrial plants are located among the municipalities of Sarnia, Corunna, Mooretown, Courtright, Sombra, and Port Lambton. Esso Petroleum, Shell Canada, Suncor, and Petrosar each have a refinery in this area.

Mercury pollution of sediments and fish is a residual problem not associated with the petroleum refinery industry. Since the source of mercury was eliminated in 1970, the levels of mercury have declined significantly.

Similarly, the PCBs in the sediment is a past problem due to spills to sewers. Now all industrial sources handle fluids which contain PCBs from transformers and capacitors according to provincial requirements.

Several sources, including the four refineries, discharge phenolic-type compounds at the rate of 0.3 to 4 kilograms per day. The provincial surface water objective for phenols (1 µg/L) is exceeded in a narrow band along the Ontario shoreline. The levels of total phenols in most of the refinery discharges are generally quite low as is evident from the companies' monthly reported data. However, according to the "Inventory of Major Municipal and

Industrial Point Source Discharges in the Great Lakes Basin" (published under the Canada-Ontario Agreement with 1980 data), the Shell Refinery at Corunna is one of two major point sources of phenols (4.4 kg/day) to the St. Clair River. Suncor is the third major contributor (2.5 kg/day). Petrosar and Imperial have extended outfalls and do not contribute to the nearshore problem.

Trace organics characteristic of refinery effluents include chloroform, methylene chloride, and other volatile chlorinated methane and ethane derivatives, aromatics including benzene/toluene and their derivatives, and polynuclear aromatic hydrocarbons (PAHs). These compounds are generally found at high levels in intermediate treatment waters but at trace concentrations in the final effluent following biological treatment (Appendix IX).

In 1978, the Ministry of the Environment completed a preliminary report entitled "Identification and Quantification of Organic Compounds: The St. Clair River Organic Study." Esso Petroleum (Imperial Oil) was found to be the third highest discharger of total organics. However, the identification and quantification of these organics require sophisticated instrumentation including gas chromatographs, mass spectrometers, and computers. For several of the trace organics identified in the 1978 report, the quantification method is still being investigated.

Five additional studies were performed on industrial discharges to the St. Clair River. When fish were exposed to industrial effluent for 48 hours, they readily accumulated trace organic compounds, some of which were either not found or found at very low levels in the effluent. The organics which appeared to bioaccumulate were aromatics, aromatic derivatives and precursors, chlorinated hydrocarbons, and polynuclear aromatic hydrocarbons. Preliminary screening for genotoxic activity using bacterial tests indicated that only one refinery effluent was non-mutagenic. These effluents should be tested more extensively using mammalian cells.

REMEDIAL ACTION

Since the phenol objective is violated in the nearshore, the refineries are required to provide diffusers which prevent the phenol from concentrating along the shoreline.

Refinery effluents in the St. Clair River are being further characterized to establish a strong data base for persistent toxic substances. The Ministry of the Environment is considering new requirements for specific organics.

MAUMEE RIVER

The following parameters are identified for this area:

Sediment Volatile Solids, COD and Metals

Fish: PCBs, DDT, Hexachlorobenzene, Chlorodane, Nonachlor, Methylbiphenyl, Methylbentanthrene, Pyridine Carboxamide, Pentachloroanisole, Heptadecane, and Nonadecane

Water: Cadmium, Iron, Manganese, Nickel, Zinc, Copper, Chromium, Dissolved Oxygen, Specific Conductivity, Phosphorus, and Fecal Coliforms

Three oil refineries discharge to this area of concern, Standard Oil and Sunoco, located in Toledo, and Standard Oil in Lima, which discharges to the Ottawa River and is 37 miles upstream from Maumee Bay. Of the above parameters, six have been identified in the discharges. At Standard Oil, Toledo, they are chemical oxygen demand, chromium, and oil and grease. At Sunoco, they are chemical oxygen demand, oil and grease, chromium, copper, zinc, and phosphorus. At Standard Oil, Lima, these are chemical oxygen demand, chromium, oil and grease, and phosphorus. The phosphorus discharge at this refinery is ten times higher than that of a typical refinery and is of some concern in view of the extensive efforts to control phosphorus in the Maumee River Basin. All of these parameters are regulated by the State of Ohio.

Of the remaining parameters, none have been specifically identified in these refineries' effluents. Some of the parameters may be present in concentrations similar to those found in a screening survey of the petroleum industry (Appendix IX).

REMEDIAL ACTION

Although the effluents from Standard Oil, Toledo and Sunoco contain parameters identified in the 1978 Great Lakes Water Quality Agreement, the levels of these parameters are at or below their NPDES permit requirements. As mentioned in the Compliance Section, Standard Oil, Lima has been required to install a new treatment system. At the present time, no additional reductions are envisioned for these facilities.

ST. LOUIS RIVER, MINNESOTA

The following parameters were identified for this area:

Sediment: TKN, Phosphorus, COD, Oil and Grease, Lead, and Iron

Fish: Mercury

Water: None

The St. Louis River was heavily polluted several years ago, but it is now classified as a Class "B" area. Of the identified parameters for this area, COD and oil and grease were found in the effluent from Murphy Oil, Superior,

Wisconsin. However, these parameters are regulated by the State of Wisconsin and the refinery is in compliance with its permit.

REMEDIAL ACTION

All of the major municipal and industrial discharges in this area have either ceased operation or are receiving adequate treatment. It is expected that sediment contaminant concentrations will decrease through natural processes.

SUMMARY

Since water pollution controls are largely based on technology and are becoming more costly to implement, the penalties for judgement errors in the decision-making process for further remedial action in areas of concern will become more unacceptable. Management of these areas will require more efficient analytical tools based on sound scientific knowledge and a practical understanding of the environmental phenomena involved. It is the opinion of the Task Force that recommendations for further remedial action for refineries (and all dischargers) in areas of concern will have to be based on analyses conducted with wasteload allocation or total maximum daily load procedures. The development of water quality models and their application to wasteload allocation analyses are, therefore, necessary components in the process of managing these areas of concern.

Toxic and Nonconventional Pollutants

As described previously (section on Effluent Limitations in the United States), the U.S. EPA conducted a sampling and analysis program at seventeen direct discharging refineries (none of which were located in the Great Lakes Basin). In Canada, Environment Canada, Ontario Ministry of the Environment, and PACE have conducted similar programs. The purpose of these programs was to determine the presence, absence, and relative concentrations of toxic pollutants from the petroleum refining industry. In the U.S., Section 307(a) of the Clean Water Act identifies the pollutants considered "toxic." This section refers to a list of 65 pollutants and categories of pollutants listed in a U.S. House of Representatives Report (Table 1, Committee Print Numbered 95-30 of the Committee on Public Works and Transportation). U.S. EPA has narrowed this list to 129 specific pollutants. This list is shown in Appendix VI. The U.S. EPA can revise the list either by adding or deleting pollutants and, in fact, has deleted three of the pollutants as noted in Appendix VI. The criteria specified in the Clean Water Act for determining whether a pollutant is toxic consists of taking into account toxicity, persistence, degradability, usual or potential presence of the affected organisms in any waters, the importance of the affected organisms, and the nature and extent of the effect of the toxic pollutant on such organisms. There are currently no other specific criteria for assessing whether a compound is toxic.

Sampling and analyses programs have been conducted to evaluate whether the toxic pollutants are present in industrial wastewaters. More recently, attempts have been made to use specific criteria to determine toxic pollutants and levels. Techniques, such as the incorporation of effluent or stream biomonitoring requirements into permits or utilization of risk-assessment procedures in determining discharge limits, are being attempted on a limited basis.

The data contained in this report results from studies conducted to determine the presence and treatability of substances identified as toxic under the Clean Water Act and certain other pollutants. Studies concerning the removal of these pollutants by biological treatment systems have been of particular interest. Summaries of the analytical results from the studies conducted on the Petroleum Refinery Industry are shown in Table 6. Detailed results are shown in Appendices IX, X, and XI.

As expected, many of the organic compounds contained in crude oil are present in the untreated wastewater. These include such pollutants as benzene, ethylbenzene, toluene, phenol, acenaphthlene, isophorone, and naphthalene. Inorganic constituents found include arsenic, chromium, copper, cyanide, and zinc.

TABLE 6. SUMMARY OF SAMPLING AND ANALYSIS RESULTS OF REFINERY EFFLUENTS STUDY

Pollutant	Intake Water µg/L	Before Biological Treatment µg/L	Effluent After Biological Treatment µg/L	Biological Treatment % Removal
Benzene	T	1706	226	87
Carbon Tetrachloride	9.0	T	6.7	
Chloroform	8.0	5.4	10.7	(-98)
Dichlorofluoromethane	5.8			
1,1 Dichloroethane	4.8		6.0	
1,2 Dichloroethane	37	65	78	(-20)
1,2 Dichloropropane	8.7	T	9.5	
Ethylbenzene	8.5	1380	7.2	>99
Methylene Chloride	32	63	45.1	28
Toluene	3.0	1802	208	88
1,1,1 Trichloroethane	3.5	114	2.7	98
Trichlorofluoromethane		3.4	5.1	(-50)
Acenaphthene		T	T	-
Acenaphthalene		T	T	-
Anthracene		0.079	0.13	(-65)
Benzo(a)Anthracene		2.7	4.2	(-56)
Benzo(k)Fluoranthene		0.26	0.1	62
Chrysene		1.74	1.3	25
Fluorene		3.9	2.4	38
Naphthalene		86	7.3	91
Phenanthrene		12	3.6	70
Pyrene			0.9	
Di-n-Butylphthalate	25		T	
Diethylphthalate	10	T	16.5	
Dimethylphthalate			14	
Bis(2-Ethylhexyl) Phthalate	125	80	11.1	86
Bis-(2-Chloroisopropyl) Ether	T		37	

TABLE 6. SUMMARY OF SAMPLING AND ANALYSIS RESULTS OF REFINERY EFFLUENTS STUDY

Pollutant	Intake Water µg/L	Before Biological Treatment µg/L	Effluent After Biological Treatment µg/L	Biological Treatment % Removal
Benzene	T	1706	226	87
Carbon Tetrachloride	9.0	T	6.7	
Chloroform	8.0	5.4	10.7	(-98)
Dichlorofluoromethane	5.8			
1,1 Dichloroethane	4.8		6.0	
1,2 Dichloroethane	37	65	78	(-20)
1,2 Dichloropropane	8.7	T	9.5	
Ethylbenzene	8.5	1380	7.2	>99
Methylene Chloride	32	63	45.1	28
Toluene	3.0	1802	208	88
1,1,1 Trichloroethane	3.5	114	2.7	98
Trichlorofluoromethane		3.4	5.1	(-50)
Acenaphthene		T	T	-
Acenaphthalene		T	T	-
Anthracene		0.079	0.13	(-65)
Benzo(a)Anthracene		2.7	4.2	(-56)
Benzo(k)Fluoranthene		0.26	0.1	62
Chrysene		1.74	1.3	25
Fluorene		3.9	2.4	38
Naphthalene		86	7.3	91
Phenanthrene		12	3.6	70
Pyrene			0.9	
Di-n-Butylphthalate	25		T	
Diethylphthalate	10	T	16.5	
Dimethylphthalate			14	
Bis(2-Ethylhexyl) Phthalate	125	80	11.1	86
Bis-(2-Chloroisopropyl) Ether	T		37	

TABLE 6 (continued)

Pollutant	Intake Water µg/L	Before Biological Treatment µg/L	Effluent After Biological Treatment µg/L	Biological Treatment % Removal
Phenol	T	1470	162	89
Polychlorinated Biphenyls		0.26	0.2	23
Hexachlorobenzene	0.011	0.07	0.03	57
Arsenic	2.0	18.0	6.0	67
Cadmium		11.0	1.0	91
Chromium	14	360	190	47
Copper	27	93	13	86
Iron	400	5,610	600	89
Lead	6.0	64	7.0	89
Mercury	0.2	0.7	0.4	43
Nickel	9.0	27	15	44
Selenium		40	7.0	82
Zinc	310	318	85	73
Barium	35	88	92	(-4)
Boron	470	349	270	22
Manganese	52	82	73	11
Fluoride	170	5,240	3,580	32
Cyanide	10	130	70	46
TOC	16,000	210,000	44,000	79
Ammonia-Nitrogen	12	13,300	6,080	54
Sulphide		5,900	1,770	70
Total Phenols	9.0	23,480	2,040	91
Oil and Grease	12,000	25,000	7,800	69

Reference: PACE Report, No. 81-4

T = Trace; () = An apparent increase was obtained, probably due to sampling and analytical variability.

However, these studies indicated that most of these pollutants were substantially reduced by the refineries existing treatment systems. In the study conducted by U.S. EPA, none of the organics in the treated effluents had an average concentration exceeding 10 µg/L, except for bis (2-ethylhexyl) phthalate and methylene chloride, both of which are contaminants of the sampling and analytical processes. Ontario, in their surveys of treated petroleum refinery effluent, found benzene, toluene, xylene, diethylbenzene and trimethylbenzene. Some of these compounds were also identified in fish. However, in the study conducted by PACE, other organic pollutants appeared in the final effluent in concentrations higher than 10 µg/L: benzene (226 µg/L); 1,2 dichloroethane (78 µg/L); toluene (208 µg/L); diethylphthalate (16.5 µg/L); dimethyl phthalate (14 µg/L); bis-(2-chloroisopropyl) ether (37 µg/L); and phenol (162 µg/L).

The reasons for the differences are not clear. Both studies related to effluents from biological treatment systems. The type and concentration of organic compounds in effluents relates to a host of factors including type and quality of crude, processes used in a refinery, final products produced as well as the treatment system in place and the overall management of the treatment facilities. Therefore, the most significant compounds in a specific refinery effluent should be verified by periodic monitoring.

Much of this final effluent data consists of results at or near the limits of detection for many of the compounds. Thus analytical variability, sampling procedures and equipment contamination have a significant effect upon the determinations. In a recent study by API (API Publication #4346 Refinery Wastewater Priority Pollutant Study), substantially different pollutant concentrations were often obtained from split samples. This anomaly was attributed to a combination of between-laboratory and within-laboratory precision and analysis of the within-laboratory variation for the two laboratories indicated that the precision was especially poor with respect to the volatile compounds.

With respect to the "persistent toxic substances" as defined in the Annex 1 of the Great Lakes Water Quality Agreement of 1978, results of the sampling and analysis of refinery effluents (which are contained in Appendices IX, X and XI) show no detection of the pesticides aldrin, dieldrin, chlordane, DDT and metabolites, endrin, heptachlor/heptachlor epoxide and toxaphene. Data for all metals and PCBs shown in Annex 1 are summarized in Table 6.

In addition to the data collected on toxics, tabulations of results on conventional and nonconventional parameters are shown in Table 7. It is important to note that all the refineries that were included in both studies were equipped with a biological treatment system.

It is anticipated that a significant portion of the toxic compounds may have accumulated in the biological sludge and some are air stripped, but this has not yet been verified. A joint refinery survey by Environment Canada and the Ontario Ministry of the Environment was completed in 1980. The results are expected to be published shortly. A joint Environment Canada/PACE Study is in progress to determine the fate of the more significant toxic compounds across a treatment system. This will include sludge characterization as well as air emission analysis from a treatment facility.

**TABLE 7. SUMMARY OF RESULTS FOR CONVENTIONAL AND
NONCONVENTIONAL POLLUTANTS**

Refinery	Bio Influent Mean	Bio Effluent Mean	% Removal
BOD₅ (mg/L)			
1	133	15	88.7
2	101	9.3	90.7
3	24	2	91.7
4	290	64	77.9
5	50	7	86.0
6	79	25	68.0
7	227	5	98.0
8	102	37	64.0
9	157	18	89.0
10	42	5	88.0
11	150	8	95.0
12	39	8	79.0
COD (mg/L)			
1	423	63.3	85.1
2	410	133	67.5
3	107	34.6	66.7
4	630	-	-
5	157	48	69.4
6	289	263	9.0
7	537	51	91.0
8	423	140	67.0
9	453	130	71.0
10	195	42	78.0
11	690	122	82.0
12	233	84	64.0
TOC (mg/L)			
1	120	16	87.0
2	103	34	70.0
3	87	11	87.4
4	183	220	-
5	43	10	76.7
6	78	89	-
7	150	24	84.0
8	137	47	66.0
9	32	25	22.0
10	54	20	63.0
11	237	41	83.0
12	67	16	76.0

Oil Spill Prevention

IN CANADA (ONTARIO)

The general provisions of both the Environmental Protection Act and the Ontario Water Resources Act prohibit the discharge of materials which may impair the environment. The Ontario Ministry of the Environment requires all spills to the environment to be dealt with promptly and effectively. Industry in general and the oil industry in particular has cooperated well with the Ministry's abatement program for spill prevention.

Direction regarding the storage of crude oil and petroleum products is provided in Ontario's Guidelines for Environmental Protection Measures at Chemical Storage Facilities, 1978. These storage guidelines apply to the storage of oil and other liquid chemicals and cover:

- containment systems - operating and maintenance;
- compatibility of liquids;
- tank location;
- drainage collection; and
- disposal of material from containment systems.

The specifics in the Design Criteria for Containment Systems includes comments upon:

- dykes;
- valves and piping;
- lagoons;
- instrumentation and alarms; and
- pumps.

In the near future, spills will be regulated under a recent amendment to the Environmental Protection Act. This amendment known as Part IX of the Act, will, when proclaimed, hold the owner as well as the person in control of a spilled pollutant (carrier, warehouse, etc.) jointly responsible for any spill. These two parties will be under legislated duty to clean up and to restore the natural environment regardless of how the spill was caused. The new Part also extends new powers to the Minister to carry out remedial measures in the event those with a duty to respond default. Municipalities are also extended the right to respond to spills and are given a right to recover costs from the owner and the person in charge of the pollutant. Those subjected to specified adverse effects are given a right to compensation. This provision is to stimulate spill prevention.

IN THE UNITED STATES

The U.S. EPA has established a regulation which provides procedures, methods, equipment, and other general requirements to prevent the discharge of

oil from nontransportation related onshore and offshore facilities into "waters of the United States." This regulation applies to facilities engaged in drilling, producing, gathering, storing, processing, refining, transferring, distributing, or consuming oil and oil products. Such facilities are required to prepare and implement a Spill Prevention Control and Countermeasure (SPCC) plan meeting specific guidelines or standards. In general the SPCC plan is a carefully thought-out plan, prepared in accordance with good engineering practices. The SPCC plan must be certified by a Registered Professional Engineer. Owners or operators required to have SPCC plans must maintain a complete copy of the plan on site.

Minimum prevention standards to keep oil from reaching water courses include:

- dikes, berms or retaining walls;
- curbing;
- culverting or other drainage systems;
- weirs, booms or barriers;
- spill diversion ponds;
- retention ponds; and
- sorbent materials.

The regulation also provides for more detailed design standards for structures located within facilities handling regulated quantities of oil. Other requirements include inspections and reports, security, and the training of personnel in spill prevention procedures.

This program, while vitally important to the petroleum refining industry, is a program separate from those regulations which establish effluent limitations for the discharge of process and storm runoff under the NPDES permit program.

Michigan requires each refinery to prepare and implement a Pollution Incident Prevention Plan administered by the Water Resources Commission. This plan requires each facility to provide selected safeguards to prevent the loss of oil, salt, and other polluting materials to the waters of the state.

In Indiana, spills of oil and other objectionable substances shall be reported, contained, and cleaned up. Regulation 330 IAC 1-6 provides for this mechanism. Civil and criminal penalties are provided and can be applied where appropriate. The state has an Emergency Response Section which investigates all reported spills and supervises the containment and cleanup.

In Ohio, oil spills are handled by Ohio EPA, Emergency Response. Spills reported to OEPA are handled in conjunction with the U.S. Coast Guard and other state, federal, or local authorities as appropriate.

In New York, under the state's Codes and Regulations, Part 610 and 611, major oil storage facilities are required to obtain a letter of certification from the state environmental agency. This Certification is valid for one year and covers locations storing greater than 400,000 gallons of oil. State law requires submission of the SPCC plan to the regional office which conducts annual inspections before issuing certification.

The state has recently proposed new regulations to cover bulk storage facilities which in addition to regulating operations involving less than 400,000 gallons of oil will also control storage of hazardous materials.

In Wisconsin, the federal requirement for the preparation and implementation of an SPCC satisfies the state requirement also.

Solid Waste Disposal

A variety of wastes are generated during the refining process and as a result of treating the effluents from these processes. There are currently four principal methods for disposing of the refinery solid wastes. These methods include land treatment (or landspreading), landfilling, lagooning, and incineration, and may be conducted either on-site or off-site, depending upon the particulars of a given operation. Traditionally, lagooning, landfilling, and incineration have been used most often, but their importance has diminished in the past two decades. Landspreading was introduced in the 1950s and has grown in importance due to its emphasis on natural biodegradation of refinery sludges.

The characteristics of oily sludges are such that soil surface microbes will, under certain conditions, decompose these wastes. For the microbes to grow, the temperature must be above 5°C. The sludge must be evenly spread. The sludge must dry on the soil surface which limits this operation to a maximum of six months of a year. Since the site must be essentially dry for spreading and working, spring runoff and rainfall will limit access. The sludge is tilled into the top six inches of soil. The microbes require nitrogen and phosphorus as well as oxygen and water to flourish and decompose these sludges. Since most crude oils are extremely low in nitrogen and phosphorus, fertilizer must be added. Besides being environmentally acceptable, this disposal method is also very economical. Wastes which are acidic or caustic or solid (catalysts, scrap iron, soot, slag, etc.) or mainly aromatic cannot be degraded by these surface microbes.

Since all refineries in the Great Lakes Basin are located on large bodies of fresh water, it is important that the soil surface biodegradation of sludges be carefully managed. Contaminated leachate or runoff produced at the site should be contained by such means as perimeter berms and drainage tiles. The possibility of the trace metals migrating into groundwater exists but can be prevented by careful site selection and operation.

A routine monitoring and recording system is used to manage the surface biodegradation site. These include piezometer wells to monitor groundwater quality at different depths and soil samples to be analyzed for oil content and trace metals.

UNITED STATES

A number of studies on the subject of solid waste disposal have been conducted by U.S. EPA and by API. In addition, attempts have been made to survey treatment and disposal practices and to estimate the costs of compliance with hazardous waste regulations.

A summary of the source of solid wastes, which were identified as part of a U.S. EPA effort to quantify atmospheric emissions from refinery solid waste handling and disposal methods, is contained in Appendix XII, Table 1.

Based upon a 1978 study, it was estimated that the 285 refineries known to be operating in the United States at that time, generated approximately 700,000 metric tons (dry weight) of solid waste annually. A breakdown of the total solid waste generation by source is shown in Appendix XII, Table 2.

Under the Resource Conservation and Recovery Act or RCRA (amendments to the Solid Waste Disposal Act), a hazardous waste is defined as a solid waste that may cause or significantly contribute to serious illness or death, or that poses a significant threat to human health or the environment when improperly managed. A waste is classified as being hazardous, and subject to regulation under RCRA, if it exhibits any one of these characteristics: ignitability, corrosivity, reactivity, or toxicity.

Based on the toxicity characteristic, five specific refinery wastes have been listed in the May 19, 1980 Federal Register as being hazardous. These five waste streams, as detailed in Appendix XII, are the dissolved air flotation skimmings, slop oil emulsion solids, heat exchanger bundle cleaning sludge, API separator sludge, and leaded gasoline tank bottoms.

The results from both U.S. EPA and API studies are presented in Appendix XII, Table 3, to provide comparisons regarding the disposal methods currently employed for refinery wastes at a number of refineries surveyed. Landspreading and landfilling appear to be the most widely employed disposal processes.

CANADA

A variety of types of wastes are produced in Canadian refineries. According to the Canadian Petroleum Refining Industry Waste Survey, 1979(6)*, 196,000 metric tons of total waste is generated yearly across Canada by the refining industry. Of this total, 61,800 metric tons are in the form of solids or semisolid waste expressed on a dry basis and 69,000 metric tons are aqueous wastes comprised mainly of spent acids and caustics. The oil content of disposed wastes is 6,200 metric tons per year or approximately .01% of the average crude refinery rate for 1979. A summary of current waste disposal practices employed by Ontario refineries is presented in Appendix XII, Table 4.

Of the waste disposal methods used across Canada, the comparative dispositions on both wet and dry basis are presented in Appendix XII, Table 5. Landspreading is particularly important for sludges and is the second frequently used in Canada on a total dry weight basis.

Characteristics of sludges spread in Canada are described in Appendix XII, Table 6. Oil sludges can vary in composition from almost no hydrocarbon components (biosludges) to moderately high hydrocarbon content (tank bottom sludge). Compared with municipal sewage sludges, refinery biosludges have similar content of metals such as copper, chromium, and mercury; more cadmium and vanadium; and less zinc, lead, nickel, and manganese. Criteria for an acceptable site as specified in Appendix XII, Table 7, are taken from a recent PACE study into the landspreading of sludges at Canadian petroleum refineries.**

*PACE, Canadian Petroleum Refining Industry Waste Survey, PACE 80-4, Oct. 1980.

**Beak Consultants Limited, Landspreading of Sludges at Canadian Petroleum Facilities, PACE 81-5A, Dec. 1981.

ONTARIO

The current trend in Canada for the disposal of sludges and liquid oily wastes is to design soil surface degradation areas within refinery property to meet company specifications and Ontario environmental protection standards. In 1981 approximately 40,300 metric tons of solid wastes were generated by Ontario refineries. Six refineries have their own surface biodegradation sites.

Waste disposal requirements are defined in several sections of the Ontario Environmental Protection Act. Whenever a disposal site is to be altered, enlarged or modified, a public hearing is held. At this public hearing, the design and operation of, and a hydrogeologic study and contingency plan for the disposal site are presented and discussed. If the Ministry agrees with these plans, a Provisional Certificate of Approval for a Waste Disposal Site is issued. This Certificate contains conditions regarding leachate monitoring, record keeping, use of vegetation grown on the site, evaluation of the monitoring data, and soil analyses. Section 45 of the Act prohibits use of the disposal land for 25 years after closure of the site. The Provisional Certificate must be registered against the land title.

WISCONSIN

The refinery in Wisconsin disposes of sludge from its treatment ponds by dewatering and removal to a municipal landfill.

NEW YORK

When in operation, the refineries in New York disposed of their API and treatment sludges in state regulated sanitary landfills.

INDIANA

Solid wastes generated from the Indiana refinery may be disposed of by two accepted means: incineration and landfill. Landfill sites must be acceptable and approved by the appropriate regulatory agencies.

Closing of Refineries

In the present period of reduced demand for petroleum products, a number of refineries have been closed. A shutdown may fall into three different categories depending on the company's plans and outlook for the future. A shutdown may be 1) temporary, with the possibility of start up in the near future, 2) permanent, with no plans for operation in the foreseeable future, or 3) permanent with plans for the refinery to be dismantled and the land put to alternate use. Some procedures are common to all cases, but it is essential to decide which course of action will be followed and to develop a detailed plan in concordance with government regulatory agencies, corporate legal counsel, and plant operations and maintenance staff. In the United States, the tenets of Resources Conservation and Recovery Act (RCRA) govern the disposal and handling procedures. In Ontario when a refinery is closed permanently, a detailed plan for closing is developed by the Ministry of the Environment and the company.

In general, when a refinery is shutdown, the charge stocks, intermediates and products are processed and shipped to market. Tank bottom sludges and residues in process vessels remain, as do solid catalysts. Under RCRA these are classified as hazardous wastes and must be treated, disposed of, or the facilities must be permitted as waste storage facilities. The sudden creation of large volumes of solid wastes may exceed the capacity of on-site treatment facilities, and some wastes may have to be disposed of off-site. Valuable catalysts in good condition may be sold to other refiners or returned to the manufacturer for recovery of the active ingredients such as platinum, cobalt, or nickel.

Atmospheric emissions are decreased significantly almost at once. Process water systems and cooling water systems are drained and processed through the existing water treatment facilities. The water treatment system must continue to operate to handle stormwater runoff from process units and tank farms until such time as the water is free of oil and other pollutants. If the shutdown is only temporary, discharge permits should remain in force. In time, treatment and disposal facilities must comply with closure procedures and past closure monitoring and care requirements of RCRA or the plan developed with Ontario, in the case of Canadian refineries.

If the refinery is to be dismantled and the site cleared for other use, disposal sites, storage pits, and any products in the subsoil must be cared for and disposed of immediately. Equipment is sold for salvage or scrap. All piping is removed and any previously undetected leaks are dealt with according to RCRA or similar requirements in Ontario.

The primary objective of these closing requirements is the protection of surface water and groundwater from deterioration while the refinery is being shutdown and dismantled. A further concern is the prevention of contamination by leaching or runoff after the site is closed.

No petroleum refiner is allowed to "abandon" a site, and each company is responsible for the proper shutdown of a facility.

Glossary of Terms

Acid extractable	Compounds extractable from acidified water using organic solvent
Additives	Chemicals added to petroleum products to enhance their performance; also, chemicals added to cooling water to prevent corrosion
Alkylation	Chemical reaction in the presence of acid to produce petroleum products such as jet fuel
API	American Petroleum Institute
Base neutral	Compounds extractable from alkaline or neutral water using organic solvent
BAT	Best Available Technology economically achievable
BCT	Best Conventional Pollutant Control Technology
Bioassay	Test in which organisms or biological systems are used to detect or measure the presence or effect of one or more substances, wastes or environmental factors alone or in combination.
Biological treatment	Use of microbes to break down waste products
BOD ₅	Five Day Biochemical Oxygen Demand
BPJ	Best Professional Judgement
BPT	Best Practicable Control Technology currently available
Catalysts	Chemicals used in the production process to increase the rate of a desired reaction
COD	Chemical Oxygen Demand
Cracking	The breakdown of large hydrocarbon molecules to smaller ones using heat
Crude oil	Raw material for a refinery. Composed of a variety of hydrocarbons.
DMR	Discharge Monitoring Report
Flash drying	Drying at lower temperature using a vacuum

GLOSSARY OF TERMS (CONTINUED)

NPDES	National Pollution Discharge Elimination System
NSPS	New Source Performance Standards
PACE	Petroleum Association for the Conservation of the Canadian Environment
PBB	Polybrominated Biphenyl
PCB	Polychlorinated Biphenyl
Petrochemical	Raw material or feedstock for synthetic organic chemicals
POTW	Publicly Owned Treatment Works
Pretreatment	Treatment provided before discharge to a municipal sewer
Production mix	Types and amounts of products at a specific refinery
PSES	Pretreatment Standards for Existing Sources
PSNS	Pretreatment Standards for New Sources
Q/A	Quality assurance
RCRA	Resource Conservation and Recovery Act
Reforming	Formation of benzene, toluene and other aromatic hydrocarbons from petroleum
Sour water	Water containing odorous sulfur compounds
SPCC	Spill Prevention Control and Countermeasure
Stream-day	Refinery operating day
Stripping	Separation of a volatile component of a liquid using gas
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
Topping	Separation of hydrocarbons by boiling in the 80°-675°F range
TSS	Total suspended solids
Waste load allocation	The procedure by which waste loadings to a receiving water body are identified, evaluated and apportioned so that water quality objectives for that water body will be met.
Waste load characterization	Identification and quantification of pollutants in an effluent

Terms of Reference

PETROLEUM REFINERY POINT SOURCE TASK FORCE

The Task Force will:

1. Identify all refineries and re-refining facilities discharging to the Great Lakes basin surface waters and through municipal treatment systems.
2. Identify all VI 1(b) requirements currently imposed by jurisdictions on refineries discharging into receiving waters and to municipal treatment systems.
3. Discuss variability and comparability between jurisdictional requirements identifying the basis of comparison as appropriate.
4. Provide historical and current loadings for regulated parameters (phosphorus and toxics in particular) and, where possible, identify projected loading changes due to new requirements and/or new or emerging technologies, emphasizing impact on the release of toxic substances.
5. Review the adequacy of self-monitoring programs to meet the above requirements.
6. Review and identify, where possible, similarities and/or differences in monitoring and analytical protocols.
7. Recommend changes in jurisdictional requirements that may be required to meet the requirements of Article VI 1(b).
8. Prepare a draft report by June 1st, 1982 for review by the Water Quality Programs Committee.

BLANK PAGE

Membership List

PETROLEUM REFINERY POINT SOURCE TASK FORCE

Mr. Thomas A. Newell
(U.S. Co-Chairman)
Assistant District Engineer
Water Quality Division, District 2
Michigan Department of Natural Resources
Lansing, MI

Mr. Jerry P. Rogers
Chemical Engineer
Compliance Section
U.S. EPA, Region V
Chicago, IL

Mr. Marvin B. Rubin
Chemical Engineer
Special Assistant to the
Assistant Administrator for Water
U.S. Environmental Protection Agency
Washington, DC

Mr. Samuel R. Via
Deputy Director, Water Pollution Control
Indiana State Board of Health
Indianapolis, IN

Mr. Joseph Reidy
Aquatic Biologist
Industrial Waste Water Section
Ohio Environmental Protection Agency
Columbus, OH

Mr. Arthur Stelzig
(Cdn. Co-Chairman)
Chief, Petroleum and Organic
Chemicals Division
Abatement and Compliance Branch
Water Pollution Directorate
Ottawa, ON

Mr. Walter P. Suboch
Head, Industrial Organics Unit
Water Resources Branch
Ontario Ministry of the Environment
Toronto, ON

Mr. Lawrence R. King
Project Officer
Pollution Control Division
Environmental Protection Service
Ontario Region
Toronto, ON

SECRETARIAT RESPONSIBILITIES

From January to May 1982
Dr. Fahmy K. Fahmy
Toxicologist

From May to October 1982
Mr. David M. Dolan
Chemical Engineer

Great Lakes Regional Office
International Joint Commission
Windsor, ON

PETROLEUM INDUSTRY TECHNICAL CONTACTS

American Petroleum Institute (API)

Mr. Raymond J. Young
American Petroleum Institute
Washington, DC

Petroleum Association for Conservation of the Canadian Environment (PACE)

Mr. Murray G. Jones
Secretary, Water Quality Committee, PACE
c/o Shell Canada Limited
Toronto, ON

Report to the
Great Lakes Water Quality Board

**A Review of the Pollution Abatement Programs
Relating to the Petroleum Refinery Industry
in the Great Lakes Basin**

Appendices

BLANK PAGE

APPENDIX I. A LIST OF PETROLEUM REFINERIES DISCHARGING DIRECTLY TO THE GREAT LAKES BASIN
UNITED STATES AND CANADA - 1981

Lake Basin and Jurisdiction Start-up Date Nominal Crude Rate Typical Effluent Rate	Processes	Product Line	Effluent Treatment
LAKE SUPERIOR			
Wisconsin			
Murphy Oil Corp., Superior 6,040 m ³ /D (38,000 bbls/D) 960 m ³ /D	Crude Unit Catalytic Cracker Hydrogen Treaters Asphalt Plant Desalting	Gasoline Diesel Fuel Liquid Propane Gas Asphalt	API Separators, Settling Pond, Aerated Lagoon, Polishing Lagoon, Sour Water Stripper
LAKE HURON			
Michigan			
Osceola Refining Company,* West Branch 1930 1,990 m ³ /D (12,500 bbls/D) 960 m ³ /D	Crude Units Atmospheric Distillation Desalting Catalytic Reformer Hydrofinishing Blending	Regular Gasoline Unleaded Gasoline JP-4 Fuel Diesel Fuel Light Fuel Oils Industrial Fuel Oil Residual Oil Kerosene	Process/Cooling/Storm Water Cooling Pond API Separator Aeration (Biological Treatment) Settling Pond

*Not in operation as of October, 1981

APPENDIX I (continued)

Lake Basin and Jurisdiction Start-up Date Nominal Crude Rate Typical Effluent Rate	Processes	Product Line	Effluent Treatment
LAKE HURON			
Michigan, cont'd.			
Total Petroleum Inc., Alma 1936 6,680 m ³ /D (42,000 bbls/D) 1,930 m ³ /D	Crude Unit Desalter Prefractionator Saturate Gas Recovery Fluid Catalytic Cracker Unsaturation Gas Recovery Alkylation Limersol Reformer (Platformers) (2) Naphtha Hydrofiners (2) Fuel Gas System Fuel Gas Amine Unit (H ₂ Stripper) Sulfur Plant Hydrofiners (2) MSO and Slurry Mercox Units LPG Extraction (2) Gasoline Sweetening (2) Heater Oil Sweetening (1)	Gasoline, Regular & No Lead #1, #2 & #6 Fuel Oil Propane Mineral Seal Oil	Process/Cooling/Storm Water API Separation Biological Treatment Pond (Aeration) Polishing Ponds Land Disposal of Biological Sludges Deep Well Disposal Selected Wastewater

APPENDIX I (continued)

Lake Basin and Jurisdiction Start-up Date Nominal Crude Rate Typical Effluent Rate	Processes	Product Line	Effluent Treatment
LAKE MICHIGAN			
Michigan			
Lakeside Refining Company Kalamazoo 1939 477 m ³ /D (3,000 bbls/D) 3,520 m ³ /D	Crude Units Pre Flash Fractionating Reflux Desalters	Gasoline Rubber Solvent JP-4 Fuel #1, #2, Fuel Oils #5 Residual Oil	Cooling Water/Storm Water API Separator Chemical Treatment Settling Filtering Cooling Pond Process Water API Separator Sanitary Sewer
Indiana			
Amoco Oil Company, Whiting 66,800 m ³ /D (420,000 bbls/D) 51,900 m ³ /D	Crude units Catalytic cracker Alkylation Hydrogen Treater	Chemical Grade Propylene LPG Leaded Regular Gasoline Unleaded Regular Gasoline Unleaded Premium Gasoline Jet Fuel Diesel #1, #2 Heater Oil Furnace Oil 4 Grades #6 Oil Industrial and Paving Asphalt Lubricating Oils Grease and Wax Light Oils Coke Sulphur	API Separation/Settling Aeration Clarification Multi-media Gravity Filtration

APPENDIX I (continued)

Lake Basin and Jurisdiction Start-up Date Nominal Crude Rate Typical Effluent Rate	Processes	Product Line	Effluent Treatment
LAKE ERIE			
Ontario			
Esso Petroleum, Sarnia 1897 20,700 m ³ /D (130,100 bbls/D) 252,000 m ³ /D	Crude units Catalytic cracker Thermal cracker Hydrocracker Catalytic reformer Aromatics extraction Alkylation Hydrogen treaters Asphalt plant Lubricating oil Wax Sulphur recovery plant	Aliphatic solvents Gasolines (auto, jet) Distillates (kerosene, stove, diesels) Heavy fuel oils Lubricating oils Wax Primary petrochemical feed Aromatics (benzene, toluene, xylenes) Asphalts Liquid Propane Gas Sulphur	<u>Treatment Equipment</u> - Effluent is separated into once-through cooling waters, sanitary wastes and phenolic/process/tank farm/storm/ship's ballast waters - Cooling waters passes through 4 parallel oil/grease separators before discharge to river - Sour waters are steam stripped of H ₂ S and NH ₃ and biologically treated in 2 units before combining with process effluent - Combined process effluent pass through 3 parallel oil/grease separators, sand/activated carbon filters and an activated sludge process before discharge to the St. Clair River - Sanitary wastes segregated and directed to Sarnia Sewage Treatment Plant
Petrosar, Corunna			
1977 27,000 m ³ /D (170,000 bbls/D) 10,000 m ³ /D	Crude Unit Hydrogen Treater Olefin/aromatics Separator Thermal cracker	Gasolines (auto) Distillates (stove, diesels) Heavy fuel oils Liquid propane gas Synthetic natural gas Aromatics (benzene, toluene, xylene)	<u>Treatment Equipment</u> - Oilly waste waters are treated by a gravity separator, equalization pond, dissolved air-oil flotation, final effluent pond - Petrochemical feedstock waters are treated by a gravity separator, equalization pond, dissolved air-oil flotation, bio-oxidation, clarification, 4 activated carbon filters, final effluent pond - Sanitary wastes are treated by extended aeration, clarification, final effluent pond - Uncontaminated storm water flows to a hold pond, then to Baby Creek - Cooling water goes to the final effluent pond - Final effluent ponds are pumped through a diffuser into the St. Clair River

APPENDIX I (continued)

Lake Basin and Jurisdiction Start-up Date Nominal Crude Rate Typical Effluent Rate	Processes	Product Line	Effluent Treatment
LAKE ERIE			
Ontario, cont'd.			
Shell Canada, Corunna 1952 11,800 m ³ /D (74,000 bbls/D) 91,300 m ³ /D	Crude unit Catalytic cracker Thermal visbreaker Hydrocracker Catalytic reformer Hydrogen treaters Catalytic polymerization Aromatics extraction Sulphur recovery plant	Aliphatic solvents Gasoline (auto) Distillates (stoves, diesels) Heavy fuel oils Primary petrochemical feed Aromatics (benzene, Sulphur	Treatment Equipment - Sour water is stripped of H ₂ S and ammonia - Waste waters - stripped sour, process, tank farm drainage, segregated storm-pass through a gravity separator - This effluent plus ship's ballast water are treated by a dissolved air - oil flotation unit - Chemical plant wastes join these wastes at the equalization basin; note untreated chemical plant wastes contain alumina, titanium and suspended solids - Combined waste are treated by a biological oxidation unit and two clarifiers - Potentially oily once-through cooling water passes through a gravity separator before combining with the treated waste waters for discharge to Telford Creek - Clean once-through cooling water is discharged directly to Telford Creek
Suncor, Sarnia 1953 14,300 m ³ /D (80,000 bbls/D) 104,000 m ³ /D	Crude units Catalytic cracker Thermal visbreaker Catalytic reformers Alkylation Hydrogen Treaters Aromatics extraction Sulphur recovery plant	Gasolines (auto, jet) Distillates (stove, diesels) Heavy fuel oils Aromatics (benzene, toluene, xylene) Liquid propane gas Sulphur	Treatment Equipment - Sour water is stripped of H ₂ S and ammonia, spent caustic neutralized and stripped of H ₂ S - Stripped sour water and process wastes are treated by gravity separator, equalization, dissolved air-oil flotation, bio-oxidation by activated sludge in an aerated basin with clarification (2 units) to an impounding basin - Once-through cooling water after gravity separation combined with the treated effluents for discharge to the St. Clair River

APPENDIX I (continued)

Lake Basin and Jurisdiction Start-up Date Nominal Crude Rate Typical Effluent Rate	Processes	Product Line	Effluent Treatment
LAKE ERIE			
Ontario, cont'd.			
Texaco Canada, Nanticoke 1977 15,900 m ³ /D (105,000 bbls/D) 3,700 m ³ /D	Crude unit Catalytic cracker Catalytic reformer Alkylation Hydrogen treaters Aromatics extraction* Sulphur Recovery Plant	Gasolines (auto, jet) Distillates (stove, diesels) Heavy fuel oils Aromatics (benzene, toluene, xylene) Liquid propane gas	<p><u>Treatment Equipment</u></p> <ul style="list-style-type: none"> - Flow rate of contaminated water through treatment system is controlled by diverting flow above design to surge pond - H₂S and ammonia are stripped from sour waters - Contaminated cooling water-blowdown is discharged to process wastes - Water - treated sour, process, ship's ballast, contaminated storm - pass through a gravity separator, equalization tanks with automatic pH control, an air flotation unit, an activated sludge plant with automatic inlet temperature control, a clarifier, recycle ponds, dual media filters to the final holding ponds, then to Lake Erie through a 400 foot submerged outfall - Clean storm water passes through a gravity separator prior to holding ponds, then to Hickory Creek and Lake Erie

*At Port Credit

APPENDIX I (continued)

Lake Basin and Jurisdiction Start-up Date Nominal Crude Rate Typical Effluent Rate	Processes	Product Line	Effluent Treatment
LAKE ERIE, CONT'D.			
Sohio, Lima 21,300 m ³ /D (134,000 bbls/D) 18,500 m ³ /D	Atmospheric and vacuum distillation Fluid catalytic cracking Catalytic reforming Hydrocracking Delayed coking Furfural extraction Dewaxing Clay contacting	Propylene, Propane, Butane, Gasoline, Jet Fuel, Kerosene, Diesel Fuel, Furnace Oil, Asphalt, Lube Oils, Heavy Fuel Oils, Coke Trolumen	Stripper to remove H ₂ and ammonia Treatment system consists of gravity separator, dissolved air flotation, two aeration zones (biological treatment), two sedimentation zones, impounding basin Treated sanitary wastes are discharged to treatment system Stripped wastes, storm water, process waters and spent cooling water treated by system Final discharge from sedimentation zones to Ottawa River
Ohio			
Sohio, Toledo 13,800 m ³ /D (87,000 bbls/D) 41,000 m ³ /D	Atmospheric crude distillation Crude desalting Vacuum crude distillation Fluid catalytic cracking Sulfuric acid alkylation Hydrocracking Hydroprocessing* Catalytic reforming Delayed coking Asphalt production	Gasoline, Furnace Oil Kerosene, Benzene, Toluene, Asphalt, Sulfur, Liquid Propane, Petroleum Spirits	Foul condensate stripper, API, separator, dissolved air flotation, biological treatment, clarification, sand filtration, gravity separator for once-through cooling water

*Hydrogen treating in the first stage of the Isocrackers.

APPENDIX I (continued)

Lake Basin and Jurisdiction Start-up Date Nominal Crude Rate Typical Effluent Rate	Processes	Product Line	Effluent Treatment
LAKE ERIE, CONT'D.			
Sun, Toledo 14,000 m ³ /D (88,000 bbls/D) 9,600 m ³ /D	Atmospheric and vacuum distillation Desalting Fluid catalytic cracking H ₂ SO ₄ alkylation Hydrocracking Hydroprocessing Catalytic reforming Catalytic polymerization Steam methane reformer Alkylate production Aromatic petrochemicals	Propane Gasoline (auto, aviation) Heavy Fuel Oils Asphalt Coke Sulfur Aromatics	All wastewater through single API separator to impounding basin for equalization, aerated in process cooling towers (biological treatment) and passed through upflow sand filter
LAKE ONTARIO			
British Petroleum, Oakville 1958 12,700 m ³ /D (78,000 bbls/D) 3,600 m ³ /D	Crude unit Catalytic cracker Catalytic reformers Alkylation Hydrogen treaters Asphalt plant	Gasolines (auto, aviation) Distillates (stove, diesel) Heavy fuel oils Asphalt Liquid propane gas Sulphur	Treatment Equipment - Flow rate through treatment system controlled - H ₂ S and ammonia stripped from sour waters before discharge to process sewer - Process, sanitary, ship's ballast wastes are treated by an oil/ grease separator, plus T.P.L., equalization basins, continuous pH adjustment, flocculation tanks, primary clarifiers, aeration tanks, clarifier and final holding lagoon, then to Lake Ontario - Storm waters pass through oil/grease separator to final holding lagoon or can be treated - Clean runoff water to final holding lagoon - Cooling water tower blowdown to final holding lagoon - One operator (part of tank farm staff) per 8-hour shift mans effluent treatment system

APPENDIX I (continued)

Lake Basin and Jurisdiction Start-up Date Nominal Crude Rate Typical Effluent Rate	Processes	Product Line	Effluent Treatment
LAKE ONTARIO			
Ontario, cont'd.			
Gulf Canada, Mississauga 1943 12,700 m ³ /D (80,100 bbls/D) 243,200 m ³ /D	Crude units Catalytic cracker Catalytic reformer Alkylation Catalytic polymerization Hydrogen treaters Hydrogen synthesis Lubricating oils Asphalt Plant Sulphur recovery plant	Aliphatic solvents Gasolines (auto, jet) Distillates (kerosene, stove, stove, diesels) Heavy fuel oils Asphalt Liquid propane gas Lubricating oils Grease Sulphur	Treatment Equipment - Gravity separator rebuilt, for compartment isolation purposes, during 1981 to allow continuous removal of sludge and to cover forebay to reduce emission of odorous compounds - H ₂ S and ammonia stripped from sour water and discharged to municipal sewer - Ballast water following gravity separator joins processed oily water in a tank for gravity separation, sand filtration and activated sludge process starting September 1982 - Once through cooling waters, three separate sewers, pass through oil skimmers - Cooling water tower blowdown, treated effluent and once through cooling water combine prior to discharge to L. Ontario - Contaminated storm waters held in 2 extremely large basins for gravity separation before discharge to Lake - Undeveloped area runoff separately discharged
Shell Canada, Bronte 1963 7,000 m ³ /D (44,000 bbls/D) 2,830 m ³ /D	Crude unit Catalytic cracker Catalytic reformer Alkylation Hydrogen treaters Sulphur recovery plant	Gasoline (auto, jet) Distillates (stove, diesel) Heavy fuel oils Liquid propane gas Sulphur	Treatment Equipment - Flow rate through treatment system controlled - Sour water stripped of H ₂ S and ammonia then combined with process wastes - Wastes-process, ballast, controlled storm - pass through a gravity separator, equalizing ponds, air flotation, preheated by steam injection for biological treatment, clarifier - Stormwater after gravity separation joins the treated effluent for more treatment in an aerated lagoon - Treated combined effluent held in a holding pond prior to discharge to Lake Ontario - One operator per 3 hour shift mans effluent treatment system

APPENDIX II. INTERMEDIATE AND FINISHED PRODUCTS
PRODUCED BY THE PETROLEUM REFINING INDUSTRY

SIC 2911*

Acid Oil
Alkylates
Aromatic Chemicals
Asphalt and Asphaltic Materials, Semisolid and Solid
Benzene
Benzol
Butadiene
Butene
Coke, Petroleum
Ethylene
Fuel Oils, Distillates and Residuals
Gas, Refinery or Still Oil
Gases, LPG Liquid Petroleum Gas
Gasoline, except Natural Gasoline
Greases, Petroleum, Lubricative, Mineral Jelly, etc.
Jet Fuels
Kerosene
Methylene
Mineral Oils, Natural
Mineral Waxes, Natural
Naphtha
Naphthenic Acids
Oils, Partly Refined
Paraffin Wax
Petrolatums, Nonmedicinal
Propylene
Road Oils
Solvents
Tar or Residuum
Toluene
Xylene

* Standard Industrial Classification

APPENDIX III. SUMMARY DESCRIPTION OF MAJOR WASTEWATER SOURCES IN REFINERIES

CRUDE OIL AND PRODUCT STORAGE

The wastewaters associated with storage of crude oil and products are mainly in the form of free and emulsified oil and suspended solids. During storage, water and suspended solids in the crude oil separate. When the water layer is drawn off, emulsified oil present at the oil-water interface is often lost to the sewers. This waste is high in COD and contains a lesser amount of BOD₅.

BALLAST WATER

The ballast waters discharged by product tankers and contaminated with product materials which are the crude feedstock in use at the refinery, and range from water soluble alcohol to residual fuels. In addition to the oil products contamination, brackish water and sediments are present, contributing high COD and dissolved solids to the refinery wastewater. These wastewaters are generally discharged to either a ballast water tank or holding ponds at the refinery. In many cases, the ballast water is discharged directly to the wastewater treatment system, and constitutes a shock load on the system.

CRUDE DESALTING

The continuous wastewater stream from a desalter contains emulsified, and occasionally, free oil, ammonia, phenol, sulfides, and suspended solids. These pollutants produce a relatively high BOD₅ and COD. This wastewater also contains enough chlorides and other dissolved materials to contribute to the dissolved solids problem in the areas where the wastewater is discharged to fresh water bodies. There are also potential thermal pollution problems because the temperature of the desalting wastewater often exceeds 95 degrees Celsius (203 degrees Fahrenheit).

CRUDE OIL FRACTIONATION

The wastewater from crude oil fractionation generally comes from three sources. The first source is the water drawn off the overhead accumulators prior to recirculation or transfer of hydrocarbons to other fractionators. This waste is a major source of sulfides and ammonia, especially when sour crudes are being processed. It also contains significant amounts of oil, chlorides, mercaptans, and phenols.

A second waste source is discharges from oil sampling lines. This oil should be separable but may form emulsions in the sewer.

A third possible waste source is the very stable oil emulsions formed in the barometric condensers used to create the reduced pressures in the vacuum distillation units. However, when barometric condensers are replaced with surface condensers, oil vapors do not come in contact with water; consequently, emulsions do not develop.

THERMAL CRACKING

The major source of wastewater in thermal cracking is the overhead accumulator on the fractionator, where water is separated from the hydrocarbon vapor and sent to the sewer system. This water usually contains various oil and oil fractions and may be high in BOD₅, COD, ammonia, phenol, and sulfides, and may be highly alkaline.

CATALYTIC CRACKING

Catalytic cracking units are one of the largest sources of sour and phenolic wastewaters in a refinery. Pollutants from catalytic cracking generally come from the steam strippers and overhead accumulators on fractionators, used to recover and separate the various hydrocarbon fractions produced in the catalytic reactors.

HYDROCRACKING

At least one wastewater stream from the process will be high in sulfides, since hydrocracking reduces the sulfur content of the material being cracked. Most of the sulfides are in the gas products which are sent to a treating unit for removal and/or recovery of sulfur and ammonia. However, in product separation and fractionation units following the hydrocracking reactor, some of the hydrogen sulfide will dissolve in the wastewater being collected. This water from the separator and fractionator will probably be high in sulfides, and possibly contain significant quantities of phenols and ammonia.

POLYMERIZATION

Polymerization is a rather dirty process in terms of pounds of pollutants per barrel of charge, but because of the small polymerization capacity in most refineries, the total waste production from the process is small. Even though the process makes use of acid catalysts, the waste stream is alkaline, because the acid catalyst in most subprocesses is recycled, and any remaining acid is removed by caustic washing. Most of the waste material comes from pretreatment of feedstock to the reactor. The wastewater is high in sulfides, mercaptans, and ammonia. These materials are removed from the feedstock in caustic acid.

ALKYLATION

The major discharge from sulfuric acid alkylation are the spent caustics from the neutralization of hydrocarbon streams leaving the sulfuric acid alkylation reactor. These wastewaters contain dissolved and suspended solids, sulfides, oils, and other contaminants. Water drawn off from the overhead accumulators contains varying amounts of oil, sulfides, and other contaminants, but is not a major source of waste in this subprocess. Most refineries process the waste sulfuric acid stream from the reactor to recover clean acids, use it as if for neutralization of other waste streams, or sell it.

Hydrofluoric (HF) acid alkylation units have small acid rerun units to purify the acid for reuse. HF units do not have a spent acid or spent caustic waste stream. Any leaks or spills that involve loss of fluorides constitute a serious and difficult pollution problem. Formation of fluorsilicates has caused line plugging and similar problems. The major sources of waste material are the overhead accumulators on the fractionator.

REFORMING

Reforming is a relatively clean process. The volume of wastewater flow is small, and none of the wastewater streams has high concentration of significant pollutants. The wastewater is alkaline, and the major pollutant is sulfide from the overhead accumulator on the stripping tower used to remove light hydrocarbon fractions from the reactor effluent. The overhead accumulator catches any water that may be contained in the hydrocarbon vapors. In addition to sulfides, the wastewater contains small amounts of ammonia, mercaptans, and oil.

SOLVENT REFINING

The major potential pollutants from the various solvent refining subprocesses are the solvents themselves. Many of the solvents, such as phenol, glycol, and amines, can produce a high BOD₅. Under ideal conditions the solvents are continually recirculated with no losses to the sewer. Unfortunately, some solvent is always lost through pump seals, flange leaks, and other sources. The main source of wastewater is from the bottom of fractionation towers.

HYDROTREATING

The strength and quantity of wastewaters generated by hydrotreating depends upon the subprocess used and feedstock. Ammonia and sulfides are the primary contaminants, but phenols may also be present if the feedstock boiling range is sufficiently high.

GREASE MANUFACTURING

Only very small volumes of wastewater are discharged from a grease manufacturing process. A small amount of oil is lost to the wastewater system through leaks in pumps. The largest waste loading occurs when the batch units are washed, resulting in soap and oil discharges to the sewer system.

ASPHALT PRODUCTION

Wastewaters from asphalt blowing contain high concentrations of oils, and have high oxygen demand. Small quantities of phenols may be present.

DRYING AND SWEETENING

The most common waste stream from drying and sweetening operations is spent caustic. The spent caustic is characterized as phenolic or sulfidic, depending on which is present in the largest concentration. Whether the spent caustic is actually phenolic or sulfidic is mainly determined by the product stream being treated. Phenolic spent caustics contain phenol, cresols,

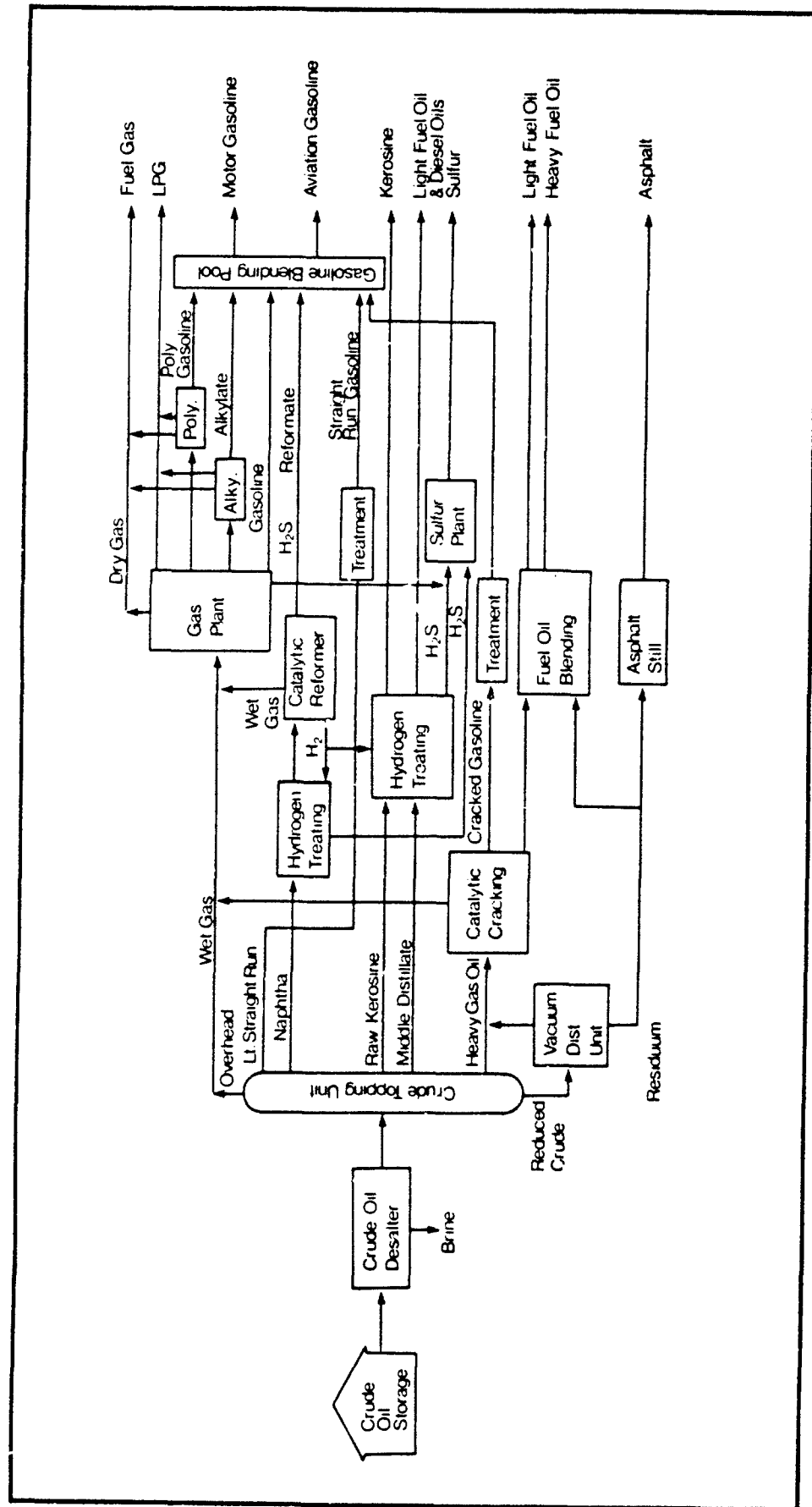
xlenols, sulfur compounds, and some neutral oils. Sulfidic spent caustics are rich in sulfides, but do not contain any phenols. These spent caustics have very high BOD₅ and COD. The phenolic caustic streams are usually sold for the recovery of phenolic materials.

Other waste streams from the process result from water washing of the treated product and regeneration of the treating solution such as sodium plumbite, Na_2PbO_2 , in doctor sweetening. These waste streams will contain small amounts of oil and the treating material such as sodium plumbite (or copper from copper chloride sweetening).

LUBE OIL FINISHING

Acid treatment of lubricating oils produces acid bearing wastes occurring as rinse waters, sludges, and discharges from sampling, leaks and shutdowns. The waste streams are also high in dissolved and suspended solids, sulfates, sulfonates, and stable oil emulsions.

Clay treatment results in only small quantities of wastewater being discharged to the sewer. Clay, free oil, and emulsified oil are the major waste constituents. However, the operation of clay recovery kilns involves potential air pollution problems of hydrocarbon and particulate emissions.



Appendix III Oil Refinery Process Flow Diagram

Appendix III



APPENDIX IV. A LIST OF PETROLEUM RE-REFINERIES
LOCATED IN THE GREAT LAKES BASIN - 1981

Lake Basin and Jurisdictions

LAKE SUPERIOR

None

LAKE HURON

None

LAKE MICHIGAN

American Recovery Company, East Chicago, IN
Mobil Oil Corporation, Milwaukee, WI

LAKE ERIE

Breslube Oil, Waterloo, ON
Dearborn Refinery Company, Dearborn, MI
Retex, Brantford, ON
Scandex, Kitchener, ON
Varnicolour, Elmira, ON

LAKE ONTARIO

Anachemia Solvents, Mississauga, ON
Booth Oil Company, Buffalo, NY
Canadian Oil Company, Toronto, ON
Monoco Oil Company, Pittsford, NY

APPENDIX V. CANADIAN EFFLUENT LIMITATIONS - FEDERAL AND ONTARIO
KILOGRAMS PER 1,000 m³ (POUNDS PER 1,000 BARRELS) OF FEEDSTOCK

Wastewater Parameters	New and Expanded or Altered Portion of Existing Refineries			Existing Refineries		
	Monthly Average	Daily Amount	Daily Maximum	Monthly Average	Daily Amount	Daily Maximum
Process and Once Through Cooling Water						
Oil and Grease	8.6 (3.0)	15.7 (5.5)	21.4 (7.5)	17.1 (6.0)	31.4 (11.0)	42.8 (15.0)
Suspended Solids	20.5 (7.2)	34.2 (12.0)	42.8 (15.0)	41.1 (14.4)	68.5 (24.0)	85.6 (30.0)
Ammonia-Nitrogen	10.3 (3.6)	16.3 (5.7)	20.5 (7.2)	14.3 (5.0)	22.8 (8.0)	28.5 (10.0)
Phenols	0.86 (0.3)	1.57 (0.55)	2.14 (0.75)	1.7 (0.6)	3.14 (1.1)	4.28 (1.5)
Sulphide	0.29 (0.1)	0.86 (0.30)	1.4 (0.5)	0.57 (0.2)	1.7 (0.6)	2.85 (1.0)
pH	-	-	6.0 - 9.5	-	-	6.0 - 9.5

95

Storm Water	Kilograms Per 1,000 m ³ of Storm Water (Pounds Per 10,000 Gals.)		Kilograms Per 1,000 m ³ of Storm Water (Pounds Per 10,000 Gals.)	
	Total, Per Month Kilograms (Pounds) Per 1000 bbls/day	Total, Per Month Kilograms (Pounds) Per 1000 bbls/day	Total, Per Month Kilograms (Pounds) Per 1000 bbls/day	Total, Per Month Kilograms (Pounds) Per 1000 bbls/day
Oil and Grease	8.8 (25.0)	0.1 (1.0)	17.5 (50.0)	0.1 (1.0)
Suspended Solids	26.3 (75.0)	0.3 (3.0)	52.6 (150.0)	0.3 (3.0)
Phenols	0.88 (2.5)	0.01 (0.1)	1.75 (5.0)	0.01 (0.1)

APPENDIX V (continued)

ACUTE TOXICITY

- Test: 96-hour flow through or 24-hour static bioassay with rainbow trout.
(The 24-hour test to be performed monthly by the refinery.)
- Criterion: 50% or greater survival in a test solution of process effluent or once through cooling water which may be diluted with up to two parts dilution water based on the refineries water usage.

DEFINITIONS

1. New Refinery
A refinery which commenced operation after October 31, 1973.
2. Existing Refinery
A refinery which commenced operation prior to November 1, 1973.
3. Expanded Refinery
An existing refinery with a Reference Crude Rate greater than 115% of the initial RCR at November 1, 1973.
4. Altered Refinery
An existing refinery which has replaced one or more of its primary atmospheric distillation towers.

ONTARIO'S LIQUID EFFLUENT GUIDELINES FOR THE PETROLEUM REFINING INDUSTRY

Introduction

The province's efforts for effluent improvement in the refining industry are directed towards the maintenance of receiving water quality which will allow for all beneficial uses and protect fish and other aquatic life. In this context, reference should be made to the published Ontario Water Management: goals, policies, objectives, and implementation procedures of the Ministry of the Environment. The water quality criteria proposed for natural waters in Ontario that are applicable to the protection of fish and aquatic life and for public surface water supplies are most significant in this case.

General Receiving Water Quality Criteria

The purpose of these guidelines is to provide general criteria which are consistent with provincial environmental management objectives.

The pertinent objectives for receiving water quality are as follows:

- The presence of visible oil in the receiving water is to be minimized.

APPENDIX V (continued)

- Contaminants that impart objectionable colour, taste, and odour to potable water supplies are to be maintained at or below their threshold concentration values. Relative to phenol, the prescribed threshold concentration values range from an average of 2 ppb to a maximum of 5 ppb (reference: objectives for the Control of Industrial Waste Discharges in Ontario).

Note: When considering effluent discharges, a minimum dilution factor 10:1 has been assumed to arrive at the effluent quality objective.

- Receiving waters are to be protected such that the dissolved oxygen levels are maintained at not less than 5 mg/L in streams supporting warm water biota or 6 mg/L in cold water streams.
- Receiving water quality should never be impaired to the point of demonstrated acute lethal, sublethal, or chronic adverse effects on important local species of aquatic life.
- Nutrient additions that stimulate the undesirable growth of algae and other objectionable plant, fungal or bacterial organisms in receiving waters are to be minimized.

ONTARIO EFFLUENT QUALITY OBJECTIVE FOR PETROLEUM REFINERIES

Oil and Grease	- 10 mg/L maximum
Phenols	- 20 µg/L maximum
Suspended Solids	- 15 mg/L maximum
Ammonia Nitrogen	- 10 mg/L maximum
COD	- 2000 mg/L maximum*
pH	- 5.5 - 9.5
Chromium	- 1 mg/L maximum
Copper	- 1 mg/L maximum
Nickel	- 1 mg/L maximum
Lead	- 1 mg/L maximum
Zinc	- 1 mg/L maximum

No froth, scum or objectionable odour or colour.

The effluent quality objectives above may be used as a basis upon which site-specific requirements are negotiated to satisfy local needs dictated by receiving stream water quality and usage.

*This is an interim objective based on the capability of current best practicable treatment technology, it may be revised as alternative technology becomes available and where dictated by demonstrated adverse effects on receiving water quality.

TOXIC AND NONCONVENTIONAL POLLUTANTS UNDER INVESTIGATION IN THE UNITED STATES SCREENING PROGRAM
APPENDIX VI.

1. acenaphthene*	Chlorinated Phenols* (Other than those listed elsewhere; includes chlorinated cresols)
2. acrolein*	
3. acrylonitrile*	
4. benzene*	21. 2,4,6-trichlorophenol
5. benzidine*	22. parachlorometa cresol
6. carbon tetrachloride* (tetrachloromethane)	23. 2-chlorophenol*
	24. chloroform* (trichloromethane)
<u>Chlorinated Benzenes* (Other than Dichlorobenzenes)</u>	<u>Dichlorobenzenes*</u>
7. chlorobenzene	25. 1,2-dichlorobenzene
8. 1,2,4-trichlorobenzene	26. 1,3-dichlorobenzene
9. hexachlorobenzene	27. 1,4-dichlorobenzene
<u>Chlorinated Ethanes*</u>	<u>Dichlorobenzidine*</u>
10. 1,2-dichloroethane	28. 3,3'-dichlorobenzidine
11. 1,1,1-trichloroethane	<u>Dichloroethylenes*</u>
12. hexachloroethane	29. 1,1-dichloroethylene
13. 1,1-dichloroethane	30. 1,2-trans-dichloroethylene
14. 1,1,2-trichloroethane	31. 2,4-dichlorophenol*
15. 1,1,2,2-tetrachloroethane	<u>Dichloropropane and Dichloropropene*</u>
16. chloroethane	32. 1,2-dichloropropane
<u>Chloroalkyl Ethers*</u>	33. 1,3-dichloropropylene (1,3-dichloropropene)
17. bis(chloromethyl) ether**	
18. bis(2-chloroethyl) ether	34. 2,4-dimethylphenol*
19. 2-chloroethyl vinyl ether (mixed)	
<u>Chlorinated Napthalene*</u>	
20. 2-chloronapthalene	

*Specific compounds and chemical classes as listed in the consent decree.

**Deleted--Federal Register, Vol. 46, No. 23 (February 4, 1981).

APPENDIX VI (continued)

Dinitrotoluene*

- 35. 2,4-dinitrotoluene
- 36. 2,6-dinitrotoluene
- 37. 1,2-diphenylhydrazine*
- 38. ethylbenzene*
- 39. fluoranthene*

Haloethers* (other than those listed elsewhere)

- 40. 4-chlorophenyl phenyl ether
- 41. 4-bromophenyl phenyl ether
- 42. bis(2-chloroisopropyl) ether
- 43. bis(2-chloroethoxy) methane

Halomethanes* (other than those listed elsewhere)

- 44. methylene chloride (dichloromethane)
- 45. methyl chloride (chloromethane)
- 46. methyl bromide (bromomethane)
- 47. bromoform (tribromomethane)
- 48. dichlorobromomethane
- 49. trichlorofluoromethane***
- 50. dichlorodifluoromethane***
- 51. chlorodibromomethane

- 52. hexachlorobutadiene*
- 53. hexachlorocyclopentadiene*
- 54. isophorone*
- 55. naphthalene*
- 56. nitrobenzene*

Nitrophenols*

- 57. 2-nitrophenol
- 58. 4-nitrophenol
- 59. 2,4-dinitrophenol*
- 60. 4,6-dinitro-o-cresol

Nitrosamines*

- 61. N-nitrosodimethylamine
- 62. N-nitrosodiphenylamine
- 63. N-nitrosodi-n-propylamine
- 64. pentachlorophenol*
- 65. phenol*

Phthalate Esters

- 66. bis(2-ethylhexyl) phthalate
- 67. butyl benzyl phthalate
- 68. Di-n-butyl phthalate
- 69. di-n-octyl phthalate
- 70. diethyl phthalate
- 71. dimethyl phthalate

Polynuclear Aromatic Hydrocarbons*

- 72. benzo (a)anthracene (1,2-benzanthracene)
- 73. benzo (A)pyrene (3,4-benzopyrene)
- 74. 3,4-benzo fluoranthene
- 75. benzo (k) fluoranthene (11,12-benzo fluoranthene)
- 76. chrysene
- 77. acenaphthalene
- 78. anthracene
- 79. benzo(ghi)perylene (1,12-benzoperylene)
- 80. fluorene
- 81. phenanthrene
- 82. dibenzo (a,h) anthracene (1,2,5,6-dibenzanthracene)
- 83. indeno (1,2,3-cd) pyrene (2,3,0-phenylene pyrene)
- 84. pyrene

- 85. tetrachloroethylene*
- 86. toluene*
- 87. trichloroethylene*
- 88. vinyl chloride* (chloroethylene)

APPENDIX VI (continued)

<u>Pesticides and Metabolites</u>		<u>Polychlorinated Biphenyls* (PCBs)</u>
89. aldrin*		106. PCB-1242 (Aroclor 1242)
90. dieldrin*		107. PCB-1254 (Aroclor 1254)
91. chlordane* (technical mixture and metabolites)		108. PCB-1221 (Aroclor 1221)
		109. PCB-1232 (Aroclor 1232)
<u>DDT and Metabolites*</u>		110. PCB-1248 (Aroclor 1248)
92. 4,4'-DDT (p,p'-DDT)		111. PCB-1260 (Aroclor 1260)
93. 4,4'-DDE (p,p'-DDE)		112. PCB-1016 (Aroclor 1016)
94. 4,4'-DDD (p,p'-DDE)		113. Toxaphene*
<u>Endosulfan and Metabolites*</u>		114. Antimony* (Total)
95. a-endosulfan-Alpha		115. Arsenic* (Total)
96. b-endosulfan-Beta		116. Asbestos* (Fibrous)
97. endosulfan sulfate		117. Beryllium* (Total)
		118. Cadmium* (Total)
<u>Endrin and Metabolites*</u>		119. Chromium* (Total)
98. endrin		120. Copper* (Total)
99. endrin aldehyde		121. Cyanide* (Total)
		122. Lead* (Total)
<u>Heptachlor and Metabolites*</u>		123. Mercury* (Total)
100. heptachlor		124. Nickel* (Total)
101. heptachlor epoxide		125. Selenium* (Total)
		126. Silver* (Total)
		127. Thallium* (Total)
		128. Zinc* (Total)
<u>Hexachlorocyclohexane* (all isomers)</u>		129. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)
102. a-BHC-Alpha		
103. b-BHC-Beta		
104. r-BHC (lindane)-Gamma		
105. g-BHC-Delta		

*Specific compounds and chemical classes as listed in the consent decree.

APPENDIX VII. UNITED STATES EFFLUENT GUIDELINES
LIMITATIONS* ARE EXPRESSED AS KILOGRAMS PER 1000m³ (LBS. PER 1000 BBLs.) OF FEEDSTOCK

Subcategory	A-Topping		B-Cracking		C-Petrochemical		D-Lube		E-Integrated	
	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.
BOD ₅	12.0 (4.21)	22.7 (7.96)	15.6 (5.47)	28.2 (9.88)	18.4 (6.45)	34.6 (12.1)	25.8 (9.04)	50.6 (17.7)	26.9 (10.1)	54.4 (19.1)
TSS	10.1 (3.54)	15.8 (5.54)	12.6 (4.42)	19.5 (6.83)	14.8 (5.19)	23.4 (8.20)	22.7 (7.96)	35.6 (12.5)	23.7 (8.31)	37.3 (13.1)
COD	60.3 (21.1)	117 41.0	109 (38.2)	210 (73.6)	109 (38.2)	210 (73.6)	187 (65.5)	360 (126)	198 (69.4)	388 (136)
Oil/Grease	3.7 (1.3)	6.9 (2.4)	4.5 (1.6)	8.4 (2.9)	5.9 (2.1)	11.1 (3.89)	8.5 (3.0)	16.2 (5.68)	9.1 (3.2)	17.1 (5.99)
Phenolics	.076 (.027)	.168 (.0589)	.10 (.035)	.21 (.074)	.12 (.042)	.25 (.088)	.184 (.0645)	.38 (.13)	.192 (.0673)	.40 (.14)
Ammonia as N	1.27 (.445)	2.81 (.985)	8.5 (3.0)	18.8 (6.59)	10.6 (3.72)	23.4 (8.20)	10.6 (3.72)	23.4 (8.20)	10.6 3.72	23.4 (8.20)
Sulfide	.068 (.024)	.149 (.0522)	.082 (.029)	.18 (.063)	.099 (.035)	.22 (.077)	.10 (.035)	.33 (.12)	.158 (.0554)	.35 (.12)
Total Chromium	.20 (.07)	.345 (.121)	.25 (.088)	.43 (.15)	.30 (.11)	.52 (.18)	.45 (.16)	.77 (.27)	.48 (.17)	.82 (.28)
Hex Chromium	.012 (.004)	.028 (.0098)	.016 (.0056)	.035 (.012)	.02 (.007)	.046 (.016)	.03 (.01)	.068 (.024)	.032 (.011)	.068 (.024)

pH - All subcategories within the range 6.0 to 9.0.

*BPT Limitations were to be achieved by July 1, 1977. New proposed regulations are pending.

It should be noted that all of the above limitations are multiplied by a unique combined factor which represents the size and the process complexity (configuration) of each given refinery under consideration. The size and process configuration factors vary within the five subcategories. Additional allocations for BOD₅, TSS, COD and oil and grease are allowed for process area storm runoff and ballast water based upon the respective flows.

APPENDIX VIII [1]. ANALYTICAL PROTOCOLS - UNITED STATES

PARAMETERS	METHOD	PAGE NUMBERS IN REFERENCE				
		EPA METHODS (1974)	APHA 14 (1976)	ASTM (1975)	US GEOLOGICAL SURVEY (1970)	OTHERS
BOD ₅	Winkler (Azide modification); Electrode method	-	543	-	C (50)	ANSI (17) 1974
TSS	Glass fibre filtration; post washing of residue	268	94	-		APHA 13 (537) 1971
COD	Dichromate reflux	20	550	472	124	AOAC 12 (610) 1975 ANSI (17) 1974
Oil/Grease	Liquid - Liquid extraction with Trichloro-trifluoro-ethane gravimetric	229	515	-	-	-
Total Phenols	Distillation followed by colorimetric (4AAP)	241	574	545	-	-
Ammonia-Nitrogen	Manual Distillation (at pH9.5) followed by nesslerization; titration electrode; automated phenolate	- 159 165 168	410 412 - 616	- 237 - -	- 116 - -	- AOAC 12 (614) 1975 - -
Sulphide	Tatrimetric-Iodine for levels greater than 1 mg per litre; methylene blue photometric	284 -	505 503	- -	154 -	- -
Chromium (Unfiltered)	Digestion followed by atomic absorption; colorimetric (diphenylcarbazide)	105 -	148 192	345 286	78 77	AOAC 12 (619) 1975 -
Chromium (Filtered)	Extraction and atomic absorption; colorimetric (diphenylcarbazide)	89,105 -	- 192	- -	76 75	- -

APPENDIX VIII [2]. ANALYTICAL PROTOCOLS - CANADA

PARAMETER	METHOD	APPROVED PROCEDURE	
		REGULATIONS AND GUIDELINES [APHA 13 (1971)]	ONTARIO: OUTLINES OF ANALYTICAL METHODS (1981)
Oil and Grease	Liquid - Liquid extraction with petroleum ether	Section 13/	-
(Solvent Extractables)	Liquid -Liquid extraction with methylene chloride	-	Laboratory Method
Total Phenols	Distillation followed by colorimetric (4AAP)	Section 222 B2C	Page 17E
Sulphide	Methylene blue photometric	Section 228 C(b)	Page 217
Ammonia-Nitrogen	Ammonium molybdate colorimetric	-	Page 217
	Direct nesslerization or distillation followed by nesslerization	Section 212	-
	Alkaline phenol-hypochlorite	-	Page 147
Total Suspended Solids	Glass fibre filtration with washing of residue	Section 224 C	Page 207
COD	Dichromate reflux	-	Page 57
Chromium	Digestion followed by atomic absorption	-	Page 67
Copper, Nickel Lead, Zinc	Digestion followed by ICP atomic emission	-	Pages 75, 95, 145

APPENDIX IX [1]. INTAKE WATER PRIORITY POLLUTANTS
SUMMARY OF U.S. EPA SCREENING PROGRAM DATA

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percentage	Average	Minimum	Maximum
Volatiles	2	Acrolein	µg/L	15	0	15	0				
	3	Acrylonitrile	µg/L	15	0	15	0				
	4	Benzene	µg/L	15	1	15	1	7	1	L 1	14
	6	Carbon Tetrachloride	µg/L	15	1	15	1	7	3	L 10	50
	7	Chlorobenzene	µg/L	15	0	15	0				
	10	1,2-Dichloroethane	µg/L	15	0	15	0				
	11	1,1,1-Trichloroethane	µg/L	15	1	15	1	7	3	N-D	50
	13	1,1-Dichloroethane	µg/L	15	0	15	0				
	14	1,1,2-Trichloroethane	µg/L	15	0	15	0				
	15	1,1,2,2-Tetrachloroethane	µg/L	15	0	15	0				
	16	Chloroethane	µg/L	15	0	15	0				
	17	Bis(Chloromethyl) Ether	µg/L	15	0	15	0				
	19	2-Chloroethyl Vinyl Ether	µg/L	15	0	15	0				
	23	Chloroform	µg/L	15	3	15	3	20	11	L 1	70
	29	1,1-Dichloroethylene	µg/L	15	0	15	0				
	30	1,2-Trans-Dichloroethylene	µg/L	15	1	15	1	7	1	N-D	11
	32	1,2-Dichloropropane	µg/L	15	0	15	0				
	33	1,3-Dichloropropylene	µg/L	15	0	15	0				
	38	Ethylbenzene	µg/L	15	0	15	0				
	44	Methylene Chloride	µg/L	15	10	15	10	67	43	L 10	130
	45	Methyl Chloride	µg/L	15	0	15	0				
	46	Methyl Bromide	µg/L	15	0	15	0				
	47	Bromoform	µg/L	15	0	15	0				
	48	Dichlorobromomethane	µg/L	15	0	15	0				
	49	Trichlorofluoromethane	µg/L	15	0	15	0				
	59	Dichlorodifluoromethane	µg/L	15	0	15	0				
	51	Chlorodibromomethane	µg/L	15	0	15	0				
	85	Tetrachloroethylene	µg/L	15	1	15	1	7	3	L 10	50
	86	Toluene	µg/L	15	0	15	0				
	87	Trichloroethylene	µg/L	15	1	15	1	7	1	L 10	20
	88	Vinyl Chloride	µg/L	15	0	15	0				

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [1] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percent	Average	Minimum	Maximum
Acid Extract	21	2,4,6-Trichlorophenol	µg/L	17	0	17	0				
	22	Parachlorometa Cresol	µg/L	17	0	17	0				
	24	2-Chlorophenol	µg/L	17	0	17	0				
	31	2,4-Dichlorophenol	µg/L	17	0	17	0				
	34	2,4-Dimethylphenol	µg/L	17	0	17	0				
	57	2-Nitrophenol	µg/L	17	0	17	0				
	58	4-Nitrophenol	µg/L	17	0	17	0				
	59	2,4-Dinitrophenol	µg/L	17	0	17	0				
	60	4,6-Dinitro-O-Cresol	µg/L	17	0	17	0				
	64	Pentachlorophenol	µg/L	17	0	17	0				
	65	Phenol	µg/L	17	2	17	2	12	1	L	10
Base-Neutrals	1	Acenaphthene	µg/L	17	2	17	2	12	2	N-D	29
	5	Benzidine	µg/L	17	0	17	0				
	8	1,2,4-Trichlorobenzene	µg/L	17	0	17	0				
Base-Neutrals	9	Hexachlorobenzene	µg/L	17	0	17	0				
	12	Hexachloroethane	µg/L	17	0	17	0				
	18	Bis(2-Chloroethyl) Ether	µg/L	17	0	17	0				
	20	2-Chloronaphthalene	µg/L	17	0	17	0				
	25	1,2-Dichlorobenzene	µg/L	17	0	17	0				
	26	1,3-Dichlorobenzene	µg/L	17	0	17	0				
	27	1,4-Dichlorobenzene	µg/L	17	0	17	0				
	28	3,3'-Dichlorobenzidine	µg/L	17	0	17	0				
	35	2,4-Dinitrotoluene	µg/L	17	0	17	0				
	36	2,6-Dinitrotoluene	µg/L	17	0	17	0				
	37	1,2-Diphenylhydrazine	µg/L	17	0	17	0				
	39	Fluoranthene	µg/L	17	2	17	2	12	2	L	1
	40	4-Chlorophenyl Ether	µg/L	17	0	17	0				29
	41	4-Bromophenyl Ether	µg/L	17	0	17	0				

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [1] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percent	Average	Minimum	Maximum
Base-Neutrals cont'd.	42	Bis(2-Chloroisopropyl) Ether	µg/L	17	0	17	0				
	43	Bis(2-Chloroethoxy) Methane	µg/L	17	0	17	0				
	52	Hexachlorobutadiene	µg/L	17	0	17	0				
	53	Hexachlorocyclopentadiene	µg/L	17	0	17	0				
	54	Isophorone	µg/L	17	0	17	0				
	55	Naphthalene	µg/L	17	2	17	2	12	L 1	N-D	2
	56	Nitrobenzene	µg/L	17	0	17	0				
	61	N-Nitrosodimethylamine	µg/L	17	0	17	0				
	62	N-Nitrosodiphenylamine	µg/L	17	0	17	0				
	63	N-Nitrosodi-N-Propylamine	µg/L	17	0	17	0				
	66	Bis-(2-Ethylhexyl) Phthalate	µg/L	17	5	17	5	29	201	N-D	1100
	67	Butyl Benzyl Phthalate	µg/L	17	0	17	0				
	68	Di-N-Butyl Phthalate	µg/L	17	4	17	4	24	3	N-D	30
	69	Di-N-Octyl Phthalate	µg/L	17	0	17	0				
	70	Diethyl Phthalate	µg/L	17	0	17	0				
	71	Dimethyl Phthalate	µg/L	17	1	17	1	6	1	N-D	20
	72	1,2-Benzanthracene	µg/L	17	0	17	0				
	73	Benzo (A)Pyrene	µg/L	17	1	17	1	6	2	N-D	33
	74	3,4-Benzofluoranthene	µg/L	17	0	17	0				
	75	11,12-Benzofluoranthene	µg/L	17	0	17	0				
	76	Chrysene	µg/L	17	1	17	1	6	3	N-D	49
	77	Acenaphthylene	µg/L	17	1	17	1	6	L 1	N-D	L 1
	78	Anthracene	µg/L	17	0	17	0				
	79	1,12-Benzoperylene	µg/L	17	0	17	0				
	80	Fluorene	µg/L	17	1	17	1	6	L 1	N-D	1
	81	Phenanthrene	µg/L	17	2	17	2	12	9	L 1	160
	82	1,2:5,6-Dibenzanthracene	µg/L	17	0	17	0				
	83	Indeno(1,2,3-C,D) Pyrene	µg/L	17	0	17	0				
	84	Pyrene	µg/L	17	2	17	2	12	8	L 1	140

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [1] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percentage	Average	Minimum	Maximum
Pesticides	89	Aldrin	µg/L	17	0	17	0				
	90	Dieldrin	µg/L	17	0	17	0				
	91	Chlordane	µg/L	17	1	17	1	6	L 1	N-D	3
	92	4,4'-DDT	µg/L	17	0	17	0				
	93	4,4'-DDE	µg/L	17	0	17	0				
	94	4,4'-DDD	µg/L	17	0	17	0				
	95	Alpha-Endosulfan	µg/L	17	0	17	0				
	96	Beta-Endosulfan	µg/L	17	0	17	0				
	97	Endosulfan Sulfate	µg/L	17	0	17	0				
	98	Endrin	µg/L	17	0	17	0				
	99	Endrin Aldehyde	µg/L	17	0	17	0				
	100	Heptachlor	µg/L	17	0	17	0				
	101	Heptachlor Epoxide	µg/L	17	0	17	0				
	102	Alpha-BHC	µg/L	17	0	17	0				
	103	Beta-BHC	µg/L	17	0	17	0				
	104	Gamma-BHC	µg/L	17	0	17	0				
	105	Delta-BHC	µg/L	17	0	17	0				
	106	PCB-1242	µg/L	17	1	17	1	6	L 1	N-D	L 1
	107	PCB-1254	µg/L	17	0	17	0				
	108	PCB-1221	µg/L	17	0	17	0				
Metals	109	PCB-1232	µg/L	17	0	17	0				
	110	PCB-1248	µg/L	17	0	17	0				
	111	PCB-1260	µg/L	17	0	17	0				
	112	PCB-1016	µg/L	17	0	17	0				
	113	Toxaphene	µg/L	17	0	17	0				
	129	TCDD	µg/L	17	0	17	0				
	114	Antimony	µg/L	17	0	17	0				
	115	Arsenic	µg/L	17	4	18	5	28	L 1	L 4	35
	117	Beryllium	µg/L	17	0	85	0				

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [1] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percentage	Average	Minimum	Maximum
Metals, cont'd.	118	Cadmium	µg/L	17	4	85	4	5	L 1	L 1	8
	119	Chromium	µg/L	17	15	85	34	40	45	L 5	3000
	120	Copper	µg/L	17	12	86	48	56	30	L 4	300
	121	Cyanide	µg/L	17	3	52	4	8	1	L 5	30
	122	Lead	µg/L	17	10	88	26	30	25	L 1	700
	123	Mercury	µg/L	16	10	69	51	74	1	N-D	7
	124	Nickel	µg/L	17	9	88	13	15	13	L 1	790
	125	Selenium	µg/L	17	6	23	10	43	2	L 6	12
	126	Silver	µg/L	17	1	85	2	2	L 1	L 1	2
	127	Thallium	µg/L	17	0	34	0				
	128	Zinc	µg/L	17	16	90	56	62	110	L 1	2820
Non-Conv. Metals	148	Hex-Chromium	µg/L	16	7	48	10	21	13	L 20	250
Misc.	167	Phenolics (4AAP0)	µg/L	17	9	48	17	35	20	L 1	230

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [2]. SEPARATOR EFFLUENT PRIORITY POLLUTANTS
SUMMARY OF U.S. EPA SCREENING PROGRAM DATA

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detect- ing	Total Samples Analyzed	Total Times Detected	Per- cent	Aver- age	Min- imum	Max- imum
Volatiles	2	Acrolein	µg/L	9	0	10	0				
	3	Acrylonitrile	µg/L	9	0	10	0				
	4	Benzene	µg/L	9	8	10	9	90	434	N-D	2434
	6	Carbon Tetrachloride	µg/L	9	0	10	0				
	7	Chlorobenzene	µg/L	9	0	10	0				
	10	1,2-Dichloroethane	µg/L	9	0	10	0				
	11	1,1,1-Trichloroethane	µg/L	9	0	10	0				
	13	1,1-Dichloroethane	µg/L	9	0	10	0				
	14	1,1,2-Trichloroethane	µg/L	9	0	10	0				
	15	1,1,2,2-Tetrachloroethane	µg/L	9	0	10	0				
	16	Chloroethane	µg/L	9	0	10	0				
	17	Bis(Chloromethyl) Ether	µg/L	9	0	10	0				
	19	2-Chloroethyl Vinyl Ether	µg/L	9	0	10	0				
	23	Chloroform	µg/L	9	5	10	6	60	20	L	100
	29	1,1-Dichloroethylene	µg/L	9	0	10	0				
	30	1,2-Trans-Dichloroethylene	µg/L	9	1	10	1	10	2	N-D	20
	32	1,2-Dichloropropane	µg/L	9	0	10	0				
	33	1,3-Dichloropropylene	µg/L	9	0	10	0				
	38	Ethylbenzene	µg/L	9	6	10	7	70	134	N-D	812
	44	Methylene Chloride	µg/L	9	8	10	9	90	228	N-D	1600
	45	Methyl Chloride	µg/L	9	0	10	0				
	46	Methyl Bromide	µg/L	9	0	10	0				
	47	Bromoform	µg/L	9	0	10	0				
	48	Dichlorobromomethane	µg/L	9	1	10	1	10	2	N-D	24
	49	Trichlorofluoromethane	µg/L	9	0	10	0				
	50	Dichlorodifluoromethane	µg/L	9	0	10	0				
	51	Chlorodibromomethane	µg/L	9	0	10	0				
	85	Tetrachloroethylene	µg/L	9	1	10	1	10	5	N-D	50

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [2] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percentage	Minimum	Maximum
Volatiles, cont'd.	86	Toluene	µg/L	9	8	10	9	90	1319	N-D 11767
	87	Trichloroethylene	µg/L	9	0	10	0			
	88	Vinyl Chloride	µg/L	9	0	10	0			
Acid Extract	21	2,4,6-Trichlorophenol	µg/L	10	0	15	0			
	22	Parachlorometa Cresol	µg/L	10	0	15	0			
	24	2-Chlorophenol	µg/L	10	0	15	0			
	31	2,4-Dichlorophenol	µg/L	10	0	15	0			
	34	2,4-Dimethylphenol	µg/L	10	0	15	0			
	57	2-Nitrophenol	µg/L	10	5	15	6	40	80	N-D 650
	58	4-Nitrophenol	µg/L	10	1	15	1	7	90	N-D 1350
	59	2,4-Dinitrophenol	µg/L	10	1	15	1	7	1	N-D 20
	60	4,6-Dinitro-0-Cresol	µg/L	10	1	15	1	7	7	N-D 110
	64	Pentachlorophenol	µg/L	10	1	15	1	7	4	N-D 60
	65	Phenol	µg/L	10	1	15	1	7	57	N-D 850
					9	15	12	80	1519	N-D 16000
Base-Neutrals	1	Acenaphthene	µg/L	10	6	15	6	40	272	N-D 3000
	5	Benzidine	µg/L	10	0	15	0			
	8	1,2,4-Trichlorobenzene	µg/L	10	0	15	0			
	9	Hexachlorobenzene	µg/L	10	0	15	0			
	12	Hexachloroethane	µg/L	10	0	15	0			
	18	Bis(2-Chloroethyl) Ether	µg/L	10	0	15	0			
	20	2-Chloronaphthalene	µg/L	10	0	15	0			
	25	1,2-Dichlorobenzene	µg/L	10	0	15	0			
	26	1,3-Dichlorobenzene	µg/L	10	0	15	0			
	27	1,4-Dichlorobenzene	µg/L	10	0	15	0			
	28	3,3'-Dichlorobenzidine	µg/L	10	0	15	0			
	35	2,4-Dinitrotoluene	µg/L	10	0	15	0			
	36	2,6-Dinitrotoluene	µg/L	10	0	15	0			
	37	1,2-Diphenylhydrazine	µg/L	10	0	15	0			

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [2] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percentage	Average	Minimum	Maximum
Base-Neutrals, cont'd.	39	Fluoranthene	µg/L	10	4	15	5	33	7	N-D	40
	40	4-Chlorophenyl Phenyl Ether	µg/L	10	0	15	0				
	41	4-Bromophenyl Phenyl Ether	µg/L	10	0	15	0				
	42	Bis(2-Chloroisopropyl) Ether	µg/L	10	0	15	0				
	43	Bis(2-Chloroethoxy) Methane	µg/L	10	0	15	0				
	52	Hexachlorobutadiene	µg/L	10	0	15	0				
	53	Hexachlorocyclopentadiene	µg/L	10	0	15	0				
	54	Isophorone	µg/L	10	1	15	1	7	237	N-D	3550
	55	Naphthalene	µg/L	10	8	15	9	60	413	N-D	3200
	56	Nitrobenzene	µg/L	10	0	15	0				
	61	N-Nitrosodimethylamine	µg/L	10	0	15	0				
	62	N-Nitrosodiphenylamine	µg/L	10	0	15	0				
	63	N-Nitrosodi-N-Propylamine	µg/L	10	0	15	0				
	66	Bis(2-Ethylhexyl) Phthalate	µg/L	10	4	15	7	47	163	N-D	700
	67	Butyl Benzyl Phthalate	µg/L	10	0	15	0				
	68	Di-N-Octyl Phthalate	µg/L	10	1	15	1	7	1	N-D	1
	69	Di-N-Octyl Phthalate	µg/L	10	0	15	0				
	70	Diethyl Phthalate	µg/L	10	1	15	1	7	1	N-D	12
	71	Dimethyl Phthalate	µg/L	10	0	15	0				
	72	1,2-Benzanthracene	µg/L	10	0	15	0				
	73	Benzo (A)Pyrene	µg/L	10	0	15	0				
	74	3,4-Benzofluoranthene	µg/L	10	0	15	0				
	75	11,12-Benzofluoranthene	µg/L	10	0	15	0				
	76	Chrysene	µg/L	10	4	15	8	53	15	L	50
	77	Acenaphthylene	µg/L	10	3	15	3	20	50	N-D	665
	78	Anthracene	µg/L	10	1	15	1	7	44	N-D	660
	79	1,12-Benzoperylene	µg/L	10	0	15	0				
	80	Fluorene	µg/L	10	2	15	3	20	43	N-D	300
	81	Phenanthrene	µg/L	10	6	15	8	53	166	N-D	1100
	82	1,2:5,6-Dibenzanthracene	µg/L	10	0	15	0				

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [2] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percentage	Average	Minimum	Maximum
Base-Neutrals, cont'd.	83	Indeno(1,2,3-C,D) Pyrene	µg/L	10	0	15	0				
	84	Pyrene	µg/L	10	2	15	2	13	2	L 1	16
Pesticides	89	Aldrin	µg/L	10	1	15	1	7	1	L 5	12
	90	Dieldrin	µg/L	10	0	15	0				
	91	Chlordane	µg/L	10	0	15	0				
	92	4,4'-DDT	µg/L	10	0	15	0				
	93	4,4'-DDE	µg/L	10	1	15	1	7	L 1	N-D	7
	94	4,4'-DDD	µg/L	10	0	15	0				
	95	Alpha-Endosulfan	µg/L	10	0	15	0				
	96	Beta-Endosulfan	µg/L	10	1	15	1	7	0	N-D	13
	97	Endosulfan Sulfate	µg/L	10	0	15	0				
	98	Endrin	µg/L	10	0	15	0				
	99	Endrin Aldehyde	µg/L	10	0	15	0				
	100	Heptachlor	µg/L	10	0	15	0				
	101	Heptachlor Epoxide	µg/L	10	0	15	0				
	102	Alpha-BHC	µg/L	10	0	15	0				
	103	Beta-BHC	µg/L	10	0	15	0				
	104	Gamma-BHC	µg/L	10	0	15	0				
	105	Delta-BHC	µg/L	10	1	15	1	7	1	L 5	12
	106	PCB-1242	µg/L	10	3	15	3	20	L 1	L 5	10
	107	PCB-1254	µg/L	10	0	15	0				
	108	PCB-1221	µg/L	10	1	15	1	7	L 1	L 1	L 10
	109	PCB-1232	µg/L	10	2	15	2	13	L 1	L 1	10
	110	PCB-1248	µg/L	10	0	15	0				
	111	PCB-1260	µg/L	10	0	15	0				
	112	PCB-1016	µg/L	10	3	15	3	20	L 1	L 2	10
	113	Toxaphene	µg/L	10	0	15	0				
	129	TCDD	µg/L	10	0	15	0				

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [2] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percent	Average	Minimum	Maximum
Metals	114	Antimony	µg/L	10	2	15	2	13	24	L	1
	115	Arsenic	µg/L	10	5	19	13	68	118	L	10
	117	Beryllium	µg/L	10	1	75	1	1	L	L	1
	118	Cadmium	µg/L	10	1	78	4	5	1	L	1
	119	Chromium	µg/L	10	10	92	80	87	702	L	5
	120	Copper	µg/L	10	8	79	61	77	64	L	4
	121	Cyanide	µg/L	10	9	47	38	81	152	L	5
	122	Lead	µg/L	10	7	81	39	48	143	L	15
	123	Mercury	µg/L	10	7	80	61	76	1	L	1
	124	Nickel	µg/L	10	7	78	17	22	22	L	1
	125	Selenium	µg/L	10	4	39	29	74	9	L	4
	126	Silver	µg/L	10	1	75	3	4	L	L	1
	127	Thallium	µg/L	10	1	40	4	10	L	L	1
	128	Zinc	µg/L	10	10	100	89	87	356	L	47
											2100
Non-Conventional Metals	148	Hex-Chromium	µg/L	9	6	42	22	52	28	L	20
	150										
Misc.	167	Phenolics (4AAPD)	µg/L	10	10	48	46	96	10795	L	520
											106000

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [3]. SEPARATOR EFFLUENT PRIORITY POLLUTANTS
SUMMARY OF EPA SCREENING PROGRAM DATA

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percentage	Average	Minimum	Maximum
Volatiles	2	Acrolein	µg/L	16	0	16	0				
	3	Acrylonitrile	µg/L	16	0	16	0				
	4	Benzene	µg/L	16	4	16	4	25	2	L	12
	6	Carbon Tetrachloride	µg/L	16	0	16	0				
	7	Chlorobenzene	µg/L	16	0	16	0				
	10	1,2-Dichloroethane	µg/L	16	0	16	0				
	11	1,1,1-Trichloroethane	µg/L	16	0	16	0				
	13	1,1-Dichloroethane	µg/L	16	0	16	0				
	14	1,1,2-Trichloroethane	µg/L	16	0	16	0				
	15	1,1,2,2-Tetrachloroethane	µg/L	16	0	16	0				
	16	Chloroethane	µg/L	16	0	16	0				
	17	Bis(Chloromethyl) Ether	µg/L	16	0	16	0				
	19	2-Chloroethyl Vinyl Ether	µg/L	16	0	16	0				
	23	Chloroform	µg/L	16	2	16	2	13	6	L	5
	29	1,1-Dichloroethylene	µg/L	16	0	16	0				66
	30	1,2-Trans-Dichloroethylene	µg/L	16	0	16	0				
	32	1,2-Dichloropropane	µg/L	16	0	16	0				
	33	1,3-Dichloropropylene	µg/L	16	0	16	0				
	38	Ethylbenzene	µg/L	16	0	16	0				
	44	Methylene Chloride	µg/L	16	11	16	11	69	33	L	100
	45	Methyl Chloride	µg/L	16	0	16	0				
	46	Methyl Bromide	µg/L	16	0	16	0				
	47	Bromoform	µg/L	16	0	16	0				
	48	Dichlorobromomethane	µg/L	16	0	16	0				
	49	Trichlorofluoromethane	µg/L	16	0	16	0				
	50	Dichlorodifluoromethane	µg/L	16	0	16	0				
	51	Chlorodibromomethane	µg/L	16	0	16	0				
	85	Tetrachloroethylene	µg/L	16	0	16	0				
	86	Toluene	µg/L	16	1	16	1	6	2	L	1
	87	Trichloroethylene	µg/L	16	0	16	0				35
	88	Vinyl Chloride	µg/L	16	0	16	0				

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [3] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percentage	Average	Minimum	Maximum
Acid Extract	21	2,4,6-Trichlorophenol	µg/L	17	0	22	0				
	22	Parachlorometa Cresol	µg/L	17	1	22	1	5	L 10	L 1	10
	24	2-Chlorophenol	µg/L	17	0	22	0				
	31	2,4-Dichlorophenol	µg/L	17	1	22	1	5	L 1	N-D	10
	34	2,4-Dimethylphenol	µg/L	17	0	22	0				
	57	2-Nitrophenol	µg/L	17	0	22	0				
	58	4-Nitrophenol	µg/L	17	0	22	0				
	59	2,4-Dinitrophenol	µg/L	17	0	22	0				
	60	4,6-Dinitro-0-Cresol	µg/L	17	0	22	0				
	64	Pentachlorophenol	µg/L	17	0	22	0				
	65	Phenol	µg/L	17	0	22	0				
Base-Neutrals	1	Acenaphthene	µg/L	17	1	22	1	5	L 1	N-D	6
	5	Benzidine	µg/L	17	0	22	0				
	8	1,2,4-Trichlorobenzene	µg/L	17	0	22	0				
	9	Hexachlorobenzene	µg/L	17	0	22	0				
	12	Hexachloroethane	µg/L	17	0	22	0				
	18	Bis(2-Chloroethyl) Ether	µg/L	17	0	22	0				
	20	2-Chloronaphthalene	µg/L	17	0	22	0				
	25	1,2-Dichlorobenzene	µg/L	17	0	22	0				
	26	1,3-Dichlorobenzene	µg/L	17	0	22	0				
	27	1,4-Dichlorobenzene	µg/L	17	0	22	0				
	28	3,3'-Dichlorobenzidine	µg/L	17	0	22	0				
	35	2,4-Dinitrotoluene	µg/L	17	0	22	0				
	36	2,6-Dinitrotoluene	µg/L	17	0	22	0				
	37	1,2-Diphenylhydrazine	µg/L	17	0	22	0				
	39	Fluoranthene	µg/L	17	0	22	0				
	40	4-Chlorophenyl Ether	µg/L	17	0	22	0				
	41	4-Bromophenyl Ether	µg/L	17	0	22	0				

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [3] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percentage	Average	Minimum	Maximum
Base-Neutrals, cont'd.	42	Bis(2-Chloroisopropyl) Ether	µg/L	17	0	22	0				
	43	Bis(2-Chloroethoxy) Methane	µg/L	17	0	22	0				
	52	Hexachlorobutadiene	µg/L	17	0	22	0				
	53	Hexachlorocyclopentadiene	µg/L	17	0	22	0				
	54	Isophorone	µg/L	17	0	22	0				
	55	Naphthalene	µg/L	17	1	22	1	5	L 1	N-D	L 1
	56	Nitrobenzene	µg/L	17	0	22	0				
	61	N-Nitrosodimethylamine	µg/L	17	0	22	0				
	62	N-Nitrosodiphenylamine	µg/L	17	0	22	0				
	63	N-Nitrosodi-N-Propylamine	µg/L	17	0	22	0				
	66	Bis(2-Ethylhexyl) Phthalate	µg/L	17	5	22	5	23	180	L 10	2000
	67	Butyl Benzyl Phthalate	µg/L	17	0	22	0				
	68	Di-N-Butyl Phthalate	µg/L	17	2	22	2	9	1	N-D	10
	69	Di-N-Octyl Phthalate	µg/L	17	0	22	0				
	70	Diethyl Phthalate	µg/L	17	3	22	3	14	1	N-D	30
	71	Dimethyl Phthalate	µg/L	17	1	22	1	5	L 1	N-D	3
	72	1,2-Benzanthracene	µg/L	17	0	22	0				
	73	Benzo (A)Pyrene	µg/L	17	2	22	2	9	L 1	N-D	3
	74	3,4-Benzofluoranthene	µg/L	17	0	22	0				
	75	11,12-Benzofluoranthene	µg/L	17	0	22	0				
	76	Chrysene	µg/L	17	3	22	3	14	L 1	L 1	1
	77	Acenaphthylene	µg/L	17	0	22	0				
	78	Anthracene	µg/L	17	0	22	0				
	79	1,12-Benzoperylene	µg/L	17	0	22	0				
	80	Fluorene	µg/L	17	0	22	0				
	81	Phenanthrene	µg/L	17	1	22	1	5	L 1	L 1	1
	82	2,15,6-Dibenzanthracene	µg/L	17	0	22	0				
	83	Indeno(1,2,3-C,D) Pyrene	µg/L	17	0	22	0				
	84	Pyrene	µg/L	17	1	22	1	5	L 1	L 1	7

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [3] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detecting	Total Samples Analyzed	Total Times Detected	Percent Average	Minimum	Maximum
Pesticides	89	Aldrin	µg/L	17	0	17	0			
	90	Dieldrin	µg/L	17	0	17	0			
	91	Chlordane	µg/L	17	0	17	0			
	92	4,4'-DDT	µg/L	17	0	17	0			
	93	4,4'-DDE	µg/L	17	0	17	0			
	94	4,4'-DDD	µg/L	17	0	17	0			
	95	Alpha-Endosulfan	µg/L	17	0	17	0			
	96	Beta-Endosulfan	µg/L	17	0	17	0			
	97	Endosulfan Sulfate	µg/L	17	0	17	0			
	98	Endrin	µg/L	17	0	17	0			
	99	Endrin Aldehyde	µg/L	17	0	17	0			
	100	Heptachlor	µg/L	17	0	17	0			
	101	Heptachlor Epoxide	µg/L	17	0	17	0			
	102	Alpha-BHC	µg/L	17	0	17	0			
	103	Beta-BHC	µg/L	17	0	17	0			
	104	Gamma-BHC	µg/L	17	0	17	0			
	105	Delta-BHC	µg/L	17	0	17	0			
	106	PCB-1242	µg/L	17	0	17	0			
	107	PCB-1254	µg/L	17	0	17	0			
	108	PCB-1221	µg/L	17	0	17	0			
	109	PCB-1232	µg/L	17	0	17	0			
	110	PCB-1248	µg/L	17	0	17	0			
	111	PCB-1260	µg/L	17	0	17	0			
	112	PCB-1016	µg/L	17	0	17	0			
	113	Toxaphene	µg/L	17	0	17	0			
	129	TCDD	µg/L	17	0	17	0			

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX IX [3] (continued)

Fraction	Par. No.	Parameter	Units	Plants Sampled	Plants Detect- ing	Total Samples Analyzed	Total Times Detected	Per- cent age	Aver- age	Min- imum	Max- imum	
Metals	114	Antimony	µg/L	17	3	17	3	18	22	L	1	370
	115	Arsenic	µg/L	17	4	21	8	38	177	L	4	900
	117	Beryllium	µg/L	17	1	84	2	2	L	L	1	2
	118	Cadmium	µg/L	17	5	86	5	6	L	L	1	20
	119	Chromium	µg/L	17	17	87	68	78	115	L	5	1230
	120	Copper	µg/L	17	12	85	46	54	23	L	4	300
	121	Cyanide	µg/L	17	8	54	26	48	39	L	5	320
	122	Lead	µg/L	17	7	87	20	23	14	L	15	211
	123	Mercury	µg/L	16	11	72	53	74	1	L	1	12
	124	Nickel	µg/L	17	7	89	20	22	8	L	1	71
	125	Selenium	µg/L	17	7	31	21	68	11	L	10	32
	126	Silver	µg/L	17	2	84	3	4	L	L	1	15
	127	Thallium	µg/L	17	2	32	5	16	1	L	1	12
	128	Zinc	µg/L	17	16	92	74	80	203	L	10	2000
Non-Conventional Metals	148	Hex-Chromium	µg/L	16	5	48	6	13	5	L	20	110
	167	Phenolics (4AAP0)	µg/L	16	14	45	34	76	16	L	10	64

L=Less Than; T=Trace; N-D=Not Detected

APPENDIX X. LIST OF PARAMETERS SELECTED FOR CANADIAN REFINERY SURVEY

PHYSICAL TESTS

pH
Suspended Solids (mg/L)
 Fixed
 Volatile
Specific Conductance (umhos/cm)
Color (APHA - CU)

MISCELLANEOUS PARAMETERS

Fluoride
Cyanide
Total organic carbon
Ammonia nitrogen

Sulfide
Total phenols
Oil and Grease

METALS

Antimony	Copper
Arsenic	Iron
Beryllium	Lead
Cadmium	Mercury
Chromium	Nickel
Selenium	Thallium
Silver	Zinc

VOLATILE ORGANIC COMPOUNDS (Purgeable Group)

Benzene
Bromodichloromethane
Carbon tetrachloride
Chloroform
Dichlorodifluoromethane

1, 1 - Dichloroethane
1, 2 - Dichloroethane
1, 1 - Dichloroethylene
1, 3 - Dichloropropene - Cis
 - Trans

Ethylbenzene
Methylene chloride
Toluene
1, 1, 1 - Trichloroethane
Trichlorofluoromethane

LIQUID/LIQUID EXTRACTABLE ORGANIC COMPOUNDS

(Base Neutral Group)

Acenaphthene
Acenaphthylene
Anthracene
Benzo (a) anthracene
Benzo (k) fluoranthene
Benzo (a) pyrene

Chrysene
Fluoranthene
Fluorene
Naphthalene
Phenanthrene
Pyrene

Butyl benzylphthalate
Di-n-butylphthalate
Diethylphthalate
Dimethylphthalate
Di-n-octylphthalate
bis-(2-ethylhexyl) phthalate
bis-(2-chloroisopropyl) ether

(Acid Group)

p-chloro-m-cresol
4, 6 - Dinitro-o-cresol
Phenol

PESTICIDES AND RELATED HALOGENATED HYDROCARBONS (Pesticide Group)

Polychlorinated biphenyl

Polychlorinated terphenyls
Polybrominated biphenyls
Toxaphene
Hexachlorobenzene

APPENDIX XI. FREQUENCY OF DETECTION AND CONCENTRATION RANGE OF ORGANIC
SUBSTANCES DETECTED IN REFINERY FINAL EFFLUENTS

COMPOUND OR METAL DETECTED	FREQUENCY OF DETECTION	CONCENTRATION			COMPOUND OR METAL NOT DETECTED
		MINIMUM (µg/L)	MAXIMUM (µg/L)	MEAN (µg/L)	
<u>PURGEABLE GROUP</u>					
Benzene	7 (50%)	Trace	770	226	Bromodichlorethane
Carbon Tetrachloride	4 (29%)	Trace	20	6.7	Dichlorofluorethane
Chloroform	11 (79%)	Trace	26	10.7	1,1-Dichloroethylene
1,1-Dichloroethane	2 (14%)	2.7	9.3	6.0	1,2-Dichloropropene
1,2-Dichloroethane	2 (14%)	16	140	78.	-cis
1,2-Dichloropropane	2 (14%)	4.0	15	9.5	-trans
Ethylbenzene	4 (29%)	Trace	23	7.2	
Methylene Chloride	12 (86%)	2.0	180	45.1	
Toluene	8 (57%)	Trace	840	208	
1,1,1-Trichloroethane	5 (36%)	Trace	5.6	2.7	
Trichlorofluoromethane	2 (14%)	4.8	5.3	5.1	
<u>BASE NEUTRAL GROUP</u>					
Acenaphthene	1 (7%)	Trace	Trace	Trace	Benzo(a) Pyrene
Acenaphthalene	1 (7%)	Trace	Trace	Trace	Fluoranthene
Anthracene	2 (14%)	Trace	0.25	0.13	Butylbenzylphthalate
Benzo(a)Anthracene	3 (21%)	Trace	9.0	4.2	Di-n-octylphthalate
Benzo(k)Fluoranthene	4 (29%)	Trace	0.1	0.10	
Chrysene	4 (29%)	Trace	2.8	1.3	
Fluorene	3 (21%)	Trace	5.1	2.4	
Naphthalene	8 (57%)	Trace	32	7.3	
Phenanthrene	4 (29%)	Trace	13	3.6	
Pyrene	5 (36%)	Trace	1.6	0.9	
Di-n-butylphthalate	1 (7%)	Trace	Trace	Trace	
Diethylphthalate	2 (14%)	12	21	16.5	
Dimethylphthalate	1 (7%)	14	14	14	
bis-(2-Ethylhexyl) Phthalate	4 (29%)	Trace	14.4	11.1	
bis-(2-Chloroisopropyl) Ether	1 (7%)	37	37	37	
<u>ACID GROUP</u>					
Phenol	6 (43%)	Trace	920	162	p-Chloro-m-cresol 4,6-Dinitro-o-cresol
<u>PESTICIDE GROUP</u>					
Polychlorinated Biphenyls	3 (21%)	0.033	0.54	0.20	Polychlorinated Terphenyls
Hexachlorobenzene	9 (65%)	Trace	0.17	0.03	Polybrominated Biphenyls Toxaphene

APPENDIX XI (continued)

COMPOUND OR METAL DETECTED	FREQUENCY OF DETECTION	CONCENTRATION			COMPOUND OR METAL NOT DETECTED
		MINIMUM (mg/L)	MAXIMUM (mg/L)	MEAN (mg/L)	
METALS					
Arsenic	12 (86%)	0.001	0.014	0.006	Antimony
Cadmium	1 (7%)	0.001	0.001	0.001	Beryllium
Chromium	12 (86%)	0.002	0.68	0.19	Silver
Copper	14 (100%)	0.003	0.037	0.013	Thallium
Iron	14 (100%)	0.24	2.35	0.60	Cobalt
Lead	10 (71%)	0.002	0.018	0.007	Vanadium
Mercury	4 (29%)	0.0002	0.0006	0.0004	
Nickel	8 (57%)	0.006	0.038	0.015	
Selenium	9 (64%)	0.001	0.024	0.007	
Zinc	14 (100%)	0.008	0.24	0.085	
Barium	14 (100%)	0.013	0.27	0.092	
Boron	14 (100%)	0.002	0.75	0.27	
Manganese	14 (100%)	0.004	0.15	0.073	
MIS. PARAMETERS					
Fluoride	14 (100%)	0.025	17.5	3.58	
Cyanide	5 (36%)	0.02	0.14	0.07	
Total Organic Carbon	14 (100%)	2	380	44	
Ammonia Nitrogen	14 (100%)	0.06	18.4	6.08	
Sulphide	6 (43%)	0.07	10.	1.77	
Total Phenols	14 (100%)	0.002	8.8	2.04	
Oil and Grease	9 (64%)	2	24	7.8	

KEY

mg/L = Milligrams per liter

FREQUENCY OF DETECTION = Defined as the number of samples in which the substance in question was detected based on 14 final effluent samples. Percentage given in brackets.

APPENDIX XII [1]
SUMMARY OF IDENTIFIED SOURCES OF REFINERY SOLID WASTE STREAMS

Stream Number	Solid Waste Stream*
1	Slop Oil Emulsion Solids
2	Silt from Storm Water Runoff
3	Heat Exchanger Bundle Cleaning Sludge
4	API Separator Sludge
5	Nonleaded Gasoline Tank Bottoms
6	Crude Tank Bottoms
7	Other Storage Tank Bottoms
8	Leaded Gasoline Tank Bottoms
9	Dissolved Air Flotation Skimmings
10	Kerosene Filter Clays
11	Other Filter Clays
12	HF Alkylation Sludge
13	Waste Bio-Sludge
14	Once-Through Cooling Water Sludge
15	Fluid Catalytic Cracker Catalyst (FCC)
16	Coke Fines
17	Spent Amines
18	Salts from Regeneration
19	Ship and Barge Ballast
20	Other

*A detailed description of each stream follows this table,
keyed by stream number.

DESCRIPTION OF REFINERY SOLID WASTE STREAMS

Stream #1. Slop Oil Emulsion Solids

Oils skimmed from the API separators and Dissolved Air Flotation (DAF) units are usually pumped to an oil recovery tank where the mixture is separated into three phases: oil, water, and emulsions. The oil is blended for reprocessing and the water is recycled to the API separator. The emulsion layer must be disposed of as a solid, or it may be further treated to break the emulsion.

Stream #2. Storm Water Silt

Silt which collects in the storm water settling basins in some refineries is periodically removed, dewatered, and disposed. The quantity of silt is usually a function of the amount of rainfall and of refinery paved area, rather than of process complexity.

Stream #3. Heat Exchanger Bundle Cleaning Sludge

Heat exchanger bundles are periodically cleaned during plant shutdown. Scale and sediment removed with cleaning solutions or by high pressure water are collected in sumps. The sludge is then flushed to special sumps or process sewers, shoveled, or vacuumed out and disposed of.

Stream #4. API Separator Sludge

Solids settle in the API separator during primary wastewater treatment for removal of free oils. These sludges are periodically removed using manual labor and vacuum trucks. API separators serve as a collection point for the oily water sewers. The bottoms, therefore, contain a mixture of all sewered wastes such as storage tank draws, desalter wastes, laboratory wastes, sample line purges along with miscellaneous chemical leaks and spills.

Stream #5 and #8. Leaded or Nonleaded Product Tank Bottoms

Solids also settle to the bottom of distillate and residual storage tanks. The characteristics of these deposited sludges will vary according to the product stored in the tank. These tanks are cleaned when there is a change in service, product specifications cannot be met, or repairs are required.

Factors known to impact the volume and composition of the various tank sludges include:

- crude type;
- distillate cut;
- type and quantity of chemical additives (e.g. lead);
- recovered oil processing methods;
- use of tank mixers;
- process unit and tank metallurgy;
- product cut treatment employed upstream of tank;
- processes used in producing gasoline blend components; and
- other distillate products.

Stream #6. Crude Tank Bottoms

Solids in crude oil accumulate at the bottom of the crude oil storage tanks. These tanks are cleaned periodically to remove the sediment. The cleaning frequency is a function of the amount of sediment in the crude oil sent to distillation units and the reduction in storage capacity. Contaminants in crude oil tank sludges vary with the characteristics of crude oil and the shipping and handling methods used prior to receipt at the refinery. The waste sludges, in general, consist of a mixture of iron, rust, clay, sand, water, sediment, oil, and wax.

Stream #9. Dissolved Air Flotation Skimmings

Following treatment in an API separator, the remaining oil and solids in the wastewater are removed by DAF units in many refineries. The process takes place in a vessel where the finely divided solids and oil particulates are brought to the surface and skimmed off for disposal. The release of air dissolved in the wastewater causes the solid and oil particulates to rise.

Stream #10. Kerosene Filter Clays and Other Filter Clays

Treatment with fixed bed clay is used to remove color bodies, chemical treatment residues and traces of moisture from product streams such as gasoline, kerosene, jet fuel, and light fuel oils. Clay is also used to treat lube oils by mixing the clay with the oil and subsequently removing it by filtration.

Stream #11. HF Alkylation Sludge

Alkylation sludges are produced by both the sulfuric acid and the hydrofluoric acid alkylation process. In most refineries spent acid from these processes will accumulate in a storage tank where sludge will settle. These sludges, containing polymerized hydrocarbons, tank scale, and sulfuric acid, are removed when the tank is cleaned or repaired. The acid sludge is usually neutralized prior to disposal.

Stream #13. Waste Bio-Sludge

In the process of biological treatment of refinery aqueous waste streams, excess bio-sludge is created which must be wasted. The waste bio-sludge has a very high water content (80 to 99 percent); therefore, it is dewatered prior to disposal. The waste generation rate is dependent upon the type of biological treatment process, operating conditions, desired level of removal, and the raw waste loads.

Stream #14. Once-Through Cooling Water Sludge

In the past, large volumes of water were pumped from readily available sources and passed through primary settling sumps or tanks prior to usage for once-through cooling. In refineries where once-through water is still used, silt must periodically be removed from the settling vessel.

Stream #15. Fluid Catalytic Cracker Catalyst Fines

Fluid catalytic cracker (FCC) catalyst is continuously regenerated by burning off the coke formed on the catalyst during the cracking process. The flue gas from the regenerator passes through a series of cyclones that recover most of the catalyst. This recovered catalyst is then returned to the reactor vessel. Because of current and future air pollution regulations, more refineries have installed electrostatic precipitators or an equivalent device to remove any catalyst fines which would otherwise be released to the atmosphere with the regenerator flue gas. These catalyst fines are disposed of or in some cases sold. They are generated on a continuous basis, but are generally disposed of intermittently.

Stream #16. Coke Fines

Coke which is produced in the course of various refinery operations, such as fluid coking and delayed coking, is sold as solid industrial fuel. Coke fines are generated intermittently, and their quantity is a function of handling techniques. A certain amount of spillage and consequent contamination with dirt results in the course of loading operations onto trucks and railroad cars for disposal.

APPENDIX XII [2]
ANNUAL SOLID WASTE GENERATION PETROLEUM REFINING INDUSTRY

Stream Number (See Table 1)	Mean Solid Waste Generation Factors (Dry Metric Tons/Year) Per 1000 Barrels/Stream Day	Total Generation (Metric Tons/Year)
1	3.37	59,380
2	7.94	139,900
3	0.039	690
4	2.90	51,090
5	0.051	900
6	0.82	14,450
7	1.22	21,500
8	0.25	4,400
9	4.32	76,110
10	0.14	2,470
11	2.55	44,930
12	1.94	34,180
13	5.55	97,790
14	0.14	2,470
15	5.64	99,370
16	2.03	35,770
17	0.001	18
18	-	-
19	-	-
20	0.13	2,290
TOTAL		687,708

APPENDIX XII [3]
DISPOSAL METHODS FOR REFINERY WASTES^a

Disposal Method	EPA Survey ^b		API Survey ^c	
	On-Site	Off-Site	On-Site	Off-Site
Landfill	5	14	47	36
Lagoon	3	2	15	4
Incineration	1	0	3	0
Land Treatment ^d	10	0	27	3

^aReported in terms of number of refineries.

^bNineteen refineries reported.

^cSeventy-five refineries reported.

^dPercent refineries using land treatment on-site plus off-site,
Jacobs 10 of 19 equal 53 percent, API 30 of 75 equals 40 percent.

Source: Engineering-Science, Inc. The 1976 API Refinery Solid Waste Survey,
April 1978.

APPENDIX XII [4]
SUMMARY OF WASTE DISPOSAL METHODS - ONTARIO REFINERIES

Waste	Disposal Method
Spent catalysts	Sold to refiners, used in cement, secure landfill
Spent caustic	Neutralize effluents, sold for phenol recovery
Leaded sludge	On-site landspreading*
API sludge	On-site landspreading, offsite secure landfill
Biological sludge	On-site landspreading, offsite landfill
Desalter sludge	On-site landspreading
Off spec. sulphur	Recovery, sale, landfill
Tank bottoms	Landfill, landspreading

*Leaded sludges are disposed of in their own government approved areas.

APPENDIX XII [5]
COMPARATIVE DISPOSITIONS OF CANADIAN REFINERY WASTES^a

Disposal Means	Wet Basis (%)	Dry Basis (%) (Excluding Aqueous Waste)
Landfill	35.7	74
Recovery/Reuse	29.7	8
Landfarm	17.8	15
Incineration	6.9	3
Deepwell	1.4	-
Other	0.5	-

^aSource: PACE 80-4, 1980

APPENDIX XII [6]

TYPES AND CHARACTERISTICS OF SLUDGES LANDSPREAD IN CANADA ^a

Sludge Type	^b (n)	Oil (wt %)		Water (wt %)		Solids (wt %)	
		Range	Average	Range	Average	Range	Average
Desalting Sludge	6 19	2-30	16.4 25.5	5-84.1	36.2 53	14.4-80	47.4 21.5
API Sludge	12 33	0-70	16.4 7.5	0-95	50.9 62	5-70	32.7 30.5
Flotation Froth	3 13	2.5	4 6	75-96	88.7 90	0-20	7.3 4
Biosludge	7	0-1	0.2 0.5	85-98	93.9	2-15	6.0
Basin Settlings	8	1-60(5)	10.5(3.4) 3	5-96.6	58.5(66.1) 75	3.4-74	31.3(30.8) 22
Storm Silt	6 9	0-10	2.2 7	0-75	25.7 35	25-100	72.2 58
Filter Backwash	2 3	10-15	12.5 11	25-75	50 66	15-60	37.5 23
Slop Emulsions	5 -	1-90	24.2 N/A	5-85	50 N/A	5-60	25.8 N/A
Cooling Water Tower Sludge	2 17	0	0 N/A	10-25	17.5 N/A	75-90	82.5 N/A
Unleaded Tank Bottom Sludge	20 27	0-100	35.3 43	0-50	7.3 12	0-90	57.5 45

^a Source: PACE 80-4 (1980)

^b n = Sample size. NOTE: First set of data are for landspread sludges of the type specified; second set of data are for all sludges of that type regardless of disposal method.

APPENDIX XII [7]
SUGGESTED SUITABLE SITE PARAMETERS FOR LANDSPREADING

Parameter	Specification	Dependent Variables
Frost-free period and/or thermal period ^a	>100 days >60 days	Larger surface area and reduced application rates for areas of short frost-free periods
Topography ^b	1-9% slope	Steeper areas require more berm and runoff protection, contour ploughing; flat sites may pond water
Soil Type (unified system) ^c	Sandy loam, clayey loam	Too much sand encourages leaching, too much clay induces hardpan and ponding
Soil permeability ^c	10 ⁻³ -10 ⁻⁶ cm/s	Moderate permeability prevents leaching and surface ponding/runoff
Cation exchange capacity (CEC) ^c	>30 meq/100g	Low CEC permits metals mobilization in groundwater
^d pH	6.0-7.5	Low pH permits metal mobilization in groundwater; very high pH may also permit metals mobilization; both extremes deter microorganisms
Depth to groundwater ^e	2.4 m 1.8 m 1.5 m 1.2 m	Sand soil Loamy sand Sandy loam Loam, silty loam, clayey loam, or clay

^aPeriod with soil temperature greater than 15°C.

^bSlope <9%: OME and OMAF (1980).

^cNorris (1980).

^dApproximate range.

^eCONCAWE (1980).

Bibliography

- "Appendix to Water Quality Board Annual Report," Great Lakes Water Quality Board, Report to International Joint Commission, November 1981.
- "Biodegradation of Organic Compounds," Ontario Ministry of the Environment, Toronto, Ontario, 1980.
- "Biological Surveys," Ontario Ministry of the Environment, Toronto, Ontario, 1968 and 1978.
- "Canadian Petroleum Refining Industry Waste Survey," Petroleum Association for the Conservation of the Canadian Environment, PACE Report No. 80-4, 1980.
- "Detection of Mutagenic Activity: Screening of Twenty-three Organic Compounds of Industrial Origin in the St. Clair River," Ontario Ministry of the Environment, Toronto, Ontario, 1979.
- "Fish Toxicity and Tainting Evaluations for Selected Industrial Effluents," Ontario Ministry of the Environment, Toronto, Ontario, 1977.
- "Great Lakes Water Quality, 1977 Annual Report," Great Lakes Water Quality Board, Report to International Joint Commission, July 1978.
- "Identification and Quantification of Organic Compounds," Ontario Ministry of the Environment, Toronto, Ontario, 1981.
- "Inventory of Major Municipal and Industrial Point Source Discharges in the Great Lakes Basin," Canada-Ontario Agreement on Great Lakes Water Quality, 1980.
- "Landspreading of Sludges at Canadian Petroleum Facilities," Beak Consultants Ltd., PACE Report No. 81-5A, 1981.
- "Methods for Chemical Analysis of Water and Wastes," U.S. Environmental Protection Agency, EPA Report No. 625/6-74-003, 1974.
- "The 1976 API Refinery Solid Waste Survey," Engineering-Science, Inc., April 1978.
- "Ontario Region Petroleum Refineries Compliance Report 1980," Environment Canada, Environmental Protection Service, Pollution Control Division (Unpublished), 1982.
- "Outlines of Analytical Methods," Ministry of the Environment (Ontario), Laboratory Services Branch, June 1981.

"Petroleum Refinery Effluent Regulations and Guidelines," Environment Canada, Environmental Protection Service, Report EPS 1-WP-74-1, January 1974.

"Refinery Wastewater Priority Pollutant Study," American Petroleum Institute, API Publication No. 4346, 1981.

"The Screening of Industrial Effluents for Genotoxic Activity," Ontario Ministry of the Environment, Toronto, Ontario, 1981.

"Status Report on Abatement of Water Pollution From the Canadian Petroleum Refining Industry - 1977," Environment Canada, Environmental Protection Service, Report EPS 3-WP-79-5, July 1979.

"Survey of Trace Substances in Canadian Petroleum Industry Effluents," Petroleum Association for Conservation of the Canadian Environment (PACE), PACE Report No. 81-4, October 1981